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Technical Assistance Document for the Calibration and Operation of Automated Ambient Non-Methane Organic Compound Analyzers

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Prepared for

Environmental Monitoring Systems Lab.
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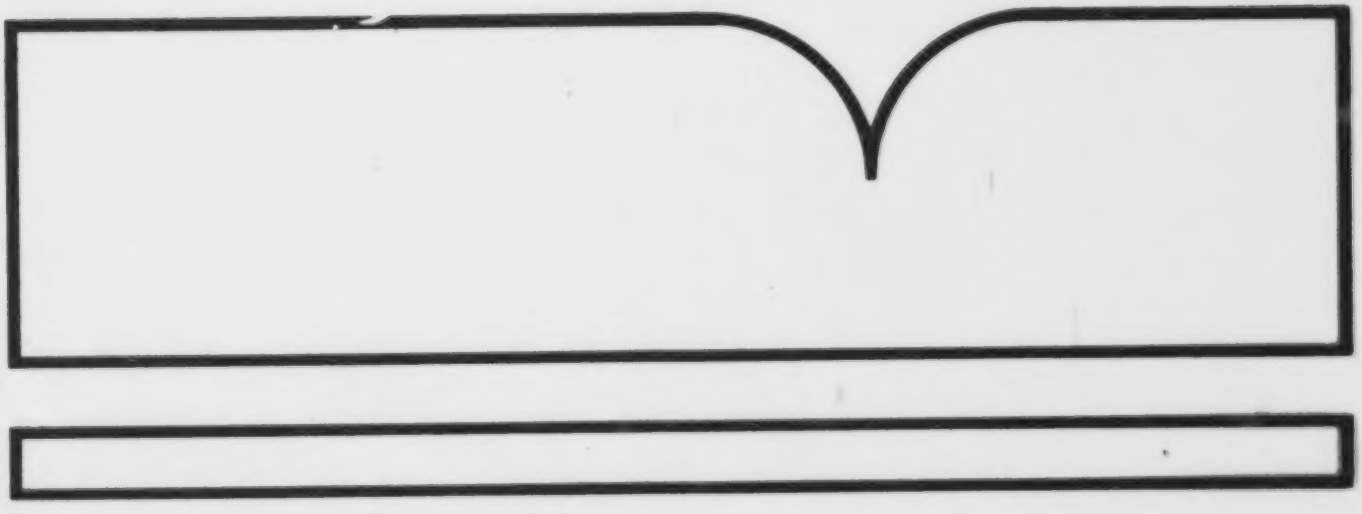

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TECHNICAL ASSISTANCE DOCUMENT FOR THE CALIBRATION AND OPERATION OF AUTOMATED AMBIENT NON-METHANE ORGANIC COMPOUND ANALYZERS

Prepared for

OFFICE OF AIR QUALITY PLANNING AND STANDARDS

Prepared by

Environmental Monitoring Systems
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This technical assistance document is intended to serve as a supplement to manufacturers' instruction manuals for automated, ambient, non-methane organic compound analyzers. It addresses augmented set-up, calibration, operation, and maintenance procedures that have been developed for the purpose of producing non-methane organic compound data suitable for use in the Empirical Kinetic Modeling Approach and other dispersion models used to predict ozone concentrations. The document initially discusses common aspects of these procedures in general terms for hydrocarbon analyzers as a whole and then specifically addresses their application to analyzers manufactured by The Bendix Corporation, Mine Safety Appliances Company, and Beckman Instruments, Inc., and Meloy Laboratories, Inc.

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FOREWORD

Measurement and monitoring research efforts are designed to anticipate potential environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations, and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina, has responsibility for: assessment of environmental monitoring technology and systems; implementation of Agency-wide quality assurance programs for air pollution measurement systems; and supplying technical support to other groups in the Agency, including the Office of Air, Noise and Radiation, the Office of Toxic Substances, and the Office of Enforcement.

Although monitoring of non-methane organic compounds (NMOC) is not required, per se, by present compliance monitoring regulations, NMOC monitoring data are vitally important in some areas for planning hydrocarbon control strategy necessary to achieve the National Ambient Air Quality Standard for ozone. Prepared at the request of the Office of Air Quality Planning and Standards (Air, Noise and Radiation), this document provides technical information and quality assurance procedures which should prove highly beneficial to control agencies making ambient NMOC measurements with automated NMOC analyzers.

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PREFACE

Although this document details problems and difficulties associated with collecting continuous non-methane organic compounds (NMOC) monitoring data, it does so to accent the need for improved quality control and better use of good laboratory procedures while operating automated NMOC analyzers. Comments contained herein are not intended to reflect invidiously on the analyzer manufacturers, authors of instruction manuals, analyzer operators, or authors of any documentation evaluating NMOC analyzers.

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ABSTRACT

This technical assistance document is intended to serve as a supplement to manufacturers' instruction manuals for automated, ambient, non-methane organic compound analyzers. It addresses augmented setup, calibration, operation, and maintenance procedures that have been developed for the purpose of producing non-methane organic compound data suitable for use in the Empirical Kinetic Modeling Approach and other dispersion models used to predict ozone concentrations. The document initially discusses common aspects of these procedures in general terms for hydrocarbon analyzers as a whole and then specifically addresses their application to analyzers manufactured by The Bendix Corporation, Mine Safety Appliances Company, and Beckman Instruments, Inc. Comments also address analyzers manufacturered by Byron Instruments, Inc., and Meloy Laboratories, Inc.

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ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

CRM	-- certified reference material
DAS	-- data acquisition system
DVM	-- digital voltmeter
EKMA	-- empirical kinetic modeling approach
EPA	-- U.S. Environmental Protection Agency
FID	-- flame ionization detector
kPa	-- kilo-Pascals
LOX	-- liquid oxygen
NAAQS	-- National Ambient Air Quality Standard
NBS	-- National Bureau of Standards
NMHC	-- non-methane hydrocarbon
NMOC	-- non-methane organic compound
psig	-- pounds per square inch
ppmC	-- parts per million as carbon
ppmV	-- parts per million by volume
RH	-- reactive hydrocarbon
SBFM	-- soap bubble flow meter
SRM	-- standard reference material
TAD	-- technical assistance document
TNMHC	-- total non-methane hydrocarbon
TOC	-- total organic compound
URL	-- upper range limit, analyzer
url	-- upper range limit, recording device
WTM	-- wet test meter

SYMBOLS

CH_4	-- methane
C_2H_4	-- ethylene
C_3H_8	-- propane
C_6H_6	-- benzene
CO_2	-- carbon dioxide
H_2	-- hydrogen
H_2O	-- water
NO_2	-- nitrogen dioxide
O_3	-- ozone
RCHO	-- aldehyde
R_2CO	-- ketone
SO_2	-- sulfur dioxide

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SECTION 1

INTRODUCTION

1.1 HYDROCARBON CHEMISTRY AND MEASUREMENT

Organic compounds containing only the elements carbon and hydrogen are called hydrocarbons. These elements can be formed into open chain aliphatic molecules (alkanes, alkenes, alkynes) or closed ring molecules (alicyclics, aromatics). Hydrocarbon compounds are frequently classified as paraffins, olefins, or aromatics. Paraffins are aliphatic compounds like propane (C_3H_8) which contain no unsaturated (multiple bonded) sites. Olefins are also aliphatic compounds, but contain one or more multiple bonds, as in ethylene (C_2H_4). Aromatics are unsaturated ring-like structures in which the benzene ring (C_6H_6) is the parent structure.

Methane (CH_4) is the simplest and most abundant hydrocarbon in the ambient air, and at common ambient concentrations it is not harmful to human health. Attention is directed primarily at the non-methane hydrocarbon compounds because these compounds are involved in photo-chemical chain reactions, resulting in an accumulation of photo-chemical oxidants in the atmosphere. Methane is not sufficiently reactive to participate appreciably in these photo-chemical reactions and can therefore be subtracted from the total hydrocarbon concentration to obtain a more accurate measure of reactive hydrocarbon concentrations. (A detailed discussion of the hydrocarbon/oxidant relationship is provided in references 1 and 2.)

The concentration resulting from the subtraction of the methane concentration from total hydrocarbon concentration has been referred to in the past as reactive hydrocarbon (RH), non-methane hydrocarbon (NMHC), and total non-methane hydrocarbon (TNMHC). A more precise reference is non-methane organic compounds (NMOC) because it includes oxygenated organics such as aldehydes (RCHO) and ketones (R_2CO) that also contribute to the buildup of photochemical oxidants. In addition, the flame ionization detector (FID) used to measure these compounds exhibits some sensitivity to oxygenated compounds. Therefore, the designation NMOC is recommended when referring to organic compounds detectable by flame ionization that contribute to the buildup of photochemical oxidants.

Concentrations of gaseous hydrocarbons have historically been reported in various units such as parts per million as carbon (ppmC), micrograms per cubic meter ($\mu g/m^3$) as methane, parts per million by volume as methane

(ppmV as CH_4), and others. To eliminate the confusion of using several units, and to normalize the response of the FID to different organics, hydrocarbon concentrations should be reported as ppmC. This unit is obtained by multiplying the ppmV concentration of the hydrocarbon compound by the number of carbon atoms in that compound. For example, 3.0 ppmV of propane (C_3H_8) is equal to 9.0 ppmC.

A National Ambient Air Quality Standard (NAAQS) for hydrocarbons corrected for methane was promulgated by the Environmental Protection Agency in 1971 (3). This NAAQS was unique among the standards promulgated at that time because it was not based upon direct harmful effects to human health or welfare caused by NMOC. Rather, the standard was based upon the role NMOC plays as a precursor to the formation of photochemical oxidants such as ozone. The standard was intended to serve as a guide for attaining the ozone NAAQS (through control of NMOC emissions) and not as a standard for compliance. More recently, photochemical models have been developed which more accurately describe the relationship between NMOC concentrations and subsequent peak ozone levels. Consequently, the original NAAQS for NMOC is no longer used.

Historically, ambient hydrocarbon concentrations have been measured by an FID. In the continuous (automated) NMOC analyzer, the sample is injected into a stream of hydrogen gas or zero air, and directed to a burner where combustion occurs. The resulting ionization of the hydrocarbons in the sample creates an electric current roughly proportional to the carbon concentration of the sample. The FID is used because it responds to a wide range of hydrocarbon compounds; is relatively insensitive to non-hydrocarbons; has a wide, linear dynamic range; and is suitable for continuous field operations.

Although the detector responds linearly to varying concentrations of individual hydrocarbons, it does not respond uniformly from one hydrocarbon species to another. For example, the response of a methane-calibrated FID to a sample of 9.0 ppmC of methane would be 9.0 ppmC, whereas its response to a sample of 9.0 ppmC of propane may be only approximately 6.3 ppmC. This non-uniform per carbon response characteristic is apparently related to the presence of the oxygen in the sample air. The FID's response to different compounds is much more uniform when the compounds are separated from the air sample by a chromatographic column, and are injected into the FID via an inert carrier gas.

In continuous NMOC analyzers, which have no columns to separate the hydrocarbons from the air, or in GC analyzers which use an air carrier, this non-uniform response to different organic compounds is a problem when attempts are made to measure the concentrations of unknown organic compounds. One method to help compensate for this effect is the judicious choice of the compound used for calibration. Accordingly, propane is recommended for the calibration of automated NMOC analyzers. Section 3.1 discusses this recommendation in more detail. Further information is also contained in reference 4.

1.2 CONTINUOUS AND DISCRETE MEASUREMENTS

Current analytical methods for obtaining NMOC measurements of ambient air can be classified as either discrete or continuous. Discrete (manual) analytical methods use a gas chromatograph with flame ionization detection (GC-FID) to quantify organic species in the sample. Because such systems are not easily transported, ambient samples are collected in inert bags or in stainless steel canisters, and are then transported to the chromatograph. The sophisticated nature of the GC system permits quantification of many individual organic compounds in the sample. The concentrations of each organic species can be summed under the categories of paraffins less methane, olefins, and aromatics. The total of these three categories, plus any unidentified organics, is the NMOC concentration. Further guidance on "sum of species" analysis is given in reference 5.

Continuous methods use automated analyzers with FIDs to provide NMOC concentrations that are generally reported as hourly averages. Such analyzers use either gas chromatographic columns to separate methane from the more complex organics, or catalytic oxidation to oxidize all organics except methane. The result is that methane and total organic compounds (TOC) are quantified by the FID separately. Subtracting methane from TOC (TOC - CH_4) gives the NMOC concentration.

Automated NMOC analyzers suffer from a number of inherent technical problems that limit the quality of data they provide. Several evaluations (6,7,8) of NMOC analyzers present a clearer assessment of these problems, and recommend potential solutions. Table 1 summarizes the problems and Table 2 summarizes the recommendations.

During the summer and fall of 1979, an evaluation (9) of NMOC analyzers was conducted to further study the quantitative effects of the problems with continuous NMOC monitoring. This evaluation pointed out that careful attention to set-up, calibration, operation, and maintenance enabled a group of commercial NMOC analyzers to produce measurements above about 0.5 ppmC which could be used in photochemical oxidation models.

1.3 PURPOSE

The purpose of this document is to supplement the instruction manuals of continuous monitoring, ambient level, NMOC analyzers. The document should be used in conjunction with the manufacturer's instruction manual so that careful attention is directed to critical procedures throughout set-up, calibration, operation, and maintenance of the NMOC analyzer. Most of the procedures recommended here were developed and evaluated during the 1979 NMOC analyzer evaluation (9). The document initially addresses these procedures in general terms for "conventional" NMOC analyzers as a whole and then specifically addresses their application to the following analyzers: MSA 11-2, Bendix 8201 and 8202, and the Beckman 6800. Comments are also made on the Byron 233 and the Meloy 500-2C. Note that the TAD is limited to

TABLE 1. SUMMARY OF PROBLEMS ASSOCIATED WITH GATHERING NMOC DATA WITH AUTOMATED ANALYZERS

1. Contaminants may be present in compressed gas cylinders containing calibration gases.
2. Compressed gas cylinders of calibration gases sometimes contain the standard in a nitrogen or argon background. When no oxygen is blended with these gases, FID sensitivity is altered.
3. The assay of calibration gases contained in compressed gas cylinders (as received from the supplier) is sometimes incorrect.
4. There are wide differences in the per-carbon response to different NMOC species.
5. FID analyzers require hydrogen, which presents a potential operational hazard.
6. The NMOC concentration is obtained by subtraction of two relatively large and nearly equal numbers ($TOC-CH_4$ = NMOC) and thus is subject to large, relative errors.
7. NMOC analyzers may exhibit excessive zero and span drift during unattended operation.
8. The complex design of some NMOC analyzers creates unique problems that are generally not experienced in other pollutant analyzers. Meticulous setup, calibration, and operation procedures (which are analyzer-specific) are difficult to understand and follow.

TABLE 2. SUMMARY OF RECOMMENDATIONS TO REDUCE THE EFFECT OF PROBLEMS LISTED IN TABLE 1

1. Calibration gases should be checked to determine the concentration of contaminants.
2. Calibration concentrations should be obtained by dynamic dilution of a pollutant standard with zero grade air containing oxygen. The dilution ratio should be sufficiently high (~ 100:1) to ensure the calibration sample contains 20.9 ± 0.3 % oxygen.
3. All calibration standards contained in compressed gas cylinders should be traceable to Standard Reference Materials from the National Bureau of Standards.
4. The NMOC response should be calibrated to a propane standard.
5. The operator should use documented procedures for hydrogen safety.
6. All channels should be properly calibrated.
7. The FIDs should be operated in accordance with instructions supplied by the manufacturer and this document.
8. The training of qualified operators should be augmented with a Technical Assistance Document, which details calibration and operation procedures for NMOC analyzers.

those "conventional" analyzers which measure TOC and CH_4 separately and derive the NMOC reading by subtraction. No effort has been made to address other types of NMOC anlyzers, such as direct-reading chromatographs.

SECTION 2

GENERAL OPERATING PROCEDURES

2.1 INTRODUCTION

The complex operation of NMOC analyzers necessitates the need for close attention to maintenance schedules and calibration procedures in order to obtain data suitable for photochemical modeling. Three separate studies (6,7,8) have documented these needs, as well as the need for less complex procedures to verify analyzer operations. The procedures discussed in this document have been selected to address these needs and to direct attention to the importance of rigid quality control procedures.

This section is intentionally general so procedures pertinent to NMOC analyzers as a whole can be collectively addressed. More specific information is contained within the individual analyzer sections located in the latter half of this document. DO NOT OVERLOOK THIS GENERAL PROCEDURES SECTION. Many suggestions detailed here must be incorporated into the monitoring program to obtain suitable NMOC data. These suggestions are not detailed in the specific analyzer sections.

2.1.1 Site Selection

Proper selection of the monitoring site has been carefully detailed in references 4, 10, and 11.

2.1.2 Analyzer Environment Control

Control of the station environment surrounding the NMOC analyzer is recommended. In a recent evaluation of NMOC analyzers (9), controllers failed (for several days) to maintain the temperature in the monitoring station within the specified range. The temperature hovered at 38° C (100° F) and resulted in poor analyzer stability, excessive noise, and erratic responses from many of the analyzers. To reduce these potential problems, the temperature range for operating NMOC analyzers should be controlled between 20 and 30° C (68 and 86° F), the temperature range in which equivalency testing of other automated methods is currently conducted. When ambient temperatures exceed about 29° C (85° F) in areas of high humidity, the sample manifold should be monitored for moisture buildup. Analyzers without moisture drop-out traps may be damaged by moisture; therefore, increase the station temperature to within 5 to 7° C (9 and 13° F) of ambient temperature if excessive moisture accumulates in the station manifold.

Power supplied to the analyzer should be between 105 and 125 volts at 60 Hz. The normal voltage range supplied to the analyzer, as well as the presence of power surges, can be determined by periodically monitoring the voltage supplied to the analyzer with a voltmeter. Typically, voltage monitoring should be performed when the site is initially set up and at the beginning of heating and cooling seasons. Elaborate systems to stabilize the electrical supply and continually record its voltage are expensive and may be unnecessary if preliminary voltmeter results indicate the voltage range is within specifications during periods of sudden high power demand.

Another factor affecting the analyzer's environment is dust. Collection of dust on electrical components can cause shorts to occur in electrical circuits; therefore, gently blow dust off electrical components every six months, or more frequently if necessary. Use a dry gas such as nitrogen or compressed air.

2.1.3 Ambient Air Sampling System

A conventional, ambient air sampling system is detailed in section 2.0.2 of EPA's QA Handbook (10); therefore, only brief comments are made here.

1. Accumulation of dirt and moisture in the sample manifold will lead to poor analyzer performance. Regularly clean the manifold when particulate or high moisture buildup is detected, and position air conditioning vents away from the manifold.

2. To ensure that the manifold blower is operating, strips of paper can be suspended in front of the blower's exhaust. The motion of the paper strips provides a visual check that the blower is operational. The blower should provide a sample flow of between 85 and 140 L/min (3 and 5 ft^3/min) through the system.

3. Ensure that the sample ports on the manifold are pointed towards the ceiling to reduce the potential for moisture accumulation in the analyzer's sample line.

4. Periodically inspect the manifold for cracks or leaks and replace as necessary to prevent sample air contamination by room air.

2.2 INSTALLATION OF NMOC ANALYZERS

NOTE: THE ANALYZER'S INSTRUCTION MANUAL AND THIS TAD SHOULD BE READ PRIOR TO SUPPLYING POWER TO THE ANALYZER.

2.2.1 Unpacking

Owners of new (and used) NMOC analyzers can avoid extended downtime by applying a few common sense procedures during unpacking. Upon receiving an analyzer, ensure that the instruction manual and Manufacturer's Final Data

Sheet are included. If they are not included, immediately notify the manufacturer. Then carefully inspect the shipping container and note the presence and location of any damage. Remove the analyzer from the box (but do not apply power to the analyzer) and determine if the exterior of the analyzer is damaged in the same general area as the shipping container. Thoroughly inspect the exterior of the analyzer for scratched surfaces, bent or broken knobs, cracked rotameters, and cracked meter covers. Inspect the interior for electronic cards which may have come unseated. Continue inspection for broken cards, loose components, loose connections, or other items which appear abnormal.

If the analyzer is obviously damaged, a shipping claim should immediately be prepared and directed to both the shipper and the manufacturer. If analyzer damage is not obvious but the shipping container shows damage, schedule ample time during start-up for a thorough equipment evaluation. Leak checks and other evaluations discussed later should be performed on analyzers suspected of having been damaged during shipping. The complexities of the NMOC analyzer necessitate proper performance of all components to insure correct operation.

2.2.2 Analyzer Instruction Manual

A complex analyzer obviously will require a thorough and sometimes complex instruction manual to describe its maintenance and operational procedures. An approach to aid the operator in understanding the instruction manual and recalling analyzer operations follows.

1. Read the instruction manual briefly and become familiar with the analyzer and the manual. Highlight all references to maintenance procedures and schedules, routine operational recordings (such as normal pressure gauge readings or rotameter readings), safety notes, and actions which can invalidate the analyzer warranty.

2. Several days later, reread the manual and fill in highlighted data on appropriate forms. (Examples of forms are given in section 2.2.3.)

3. Summarize power-up and power-down operations and calibration procedures on a step-by-step basis. A brief summary which should be prominently displayed in the analyzer area can be obtained from the manual and/or this TAD. Some instruction manuals contain condensed start-up sheets that will serve this purpose if a clear understanding of the analyzer operation has first been obtained.

2.2.3 Recordkeeping

To aid in the operation of an NMOC analyzer, records and documents should be organized and kept close at hand. Maintaining awareness of

operating parameters and maintenance schedules is important to the continuing, accurate operation of an NMOC analyzer. Detailed descriptions of recordkeeping for air monitoring programs are contained in section 2.0.3 of the EPA QA Handbook (10).

An analyzer logbook is a typical recordkeeping system. The logbook contains important records which enable the operator to recognize patterns in the analyzer's behavior and anticipate potential difficulties. Such a logbook can be contained in a ring binder and should be located at the monitoring site near the analyzer. Typical sections which should be contained in the logbook follow.

1. Instruction manual. Punch the manual (or a copy of it) to fit the rings and secure it into the binder.

2. Analyzer information. Identify the manufacturer, the analyzer's name and model number, pollutant monitored, serial number, date purchased and cost, salesperson's name and phone number, serviceperson's name and phone number, and recorder make, model and serial number (Table 3).

3. Routine check sheet. During routine checks, record operational information (Table 4).

4. Calibration data - Identify the analyzer make, model and serial number; name of operator and date of calibration; pollutant concentration, analyzer responses, and the resulting calibration curve (Table 5).

5. Zero and span data. Identify the analyzer make, model and serial number, the date, zero response, span response, span concentration, slope and intercept (Table 6).

6. Maintenance. Identify the analyzer make, model and serial number, the maintenance required, when it is required, and when it is performed (Table 7).

7. Comments. Record all comments relating to the analyzer, such as manufacturer communications, analyzer malfunctions, etc. Record the analyzer make, model and serial number at the top of <u>each</u> page and date each comment. The first page should be the Manufacturer's Final Data Sheet.

TABLE 3. FORM FOR RECORDING ANALYZER INFORMATION

Manufacturer	_____
Model	_____
Pollutant	_____
Serial Number	_____
Date Purchased	_____
Cost	$_____
Salesperson's Name	_____
Saleperson's Address	_____
Salesperson's Phone No.	_____
Serviceperson's Name	_____
Serviceperson's Address	_____
Serviceperson's Phone No.	_____
Recorder Make	_____
Recorder Model	_____
Recorder S/N	_____
Instrument Output	_____

TABLE 4. TYPICAL FORM FOR RECORDING ROUTINE OPERATIONAL DATA FROM AN NMOC ANALYZER

Day	Zero Response						Span Response						Span Gas / Conc.	% Diff.			Zero Pot Setting						Span Pot Setting						Pressure Gauges			Recorder Zero
	Unadjusted			Adjusted			Unadjusted			Adjusted							Unadjusted			Adjusted			Unadjusted			Adjusted			Air		H_2	
	TOC	CH_4	NMOC	TOC	CH_4	NMOC	TOC	CH_4	NMOC	TOC	CH_4	NMOC		TOC	CH_4	NMOC	TOC	CH_4	NMOC	TOC	CH_4	NMOC	TOC	CH_4	NMOC	TOC	CH_4	NMOC	Burner	Carrier		

MONTH

TABLE 5. FORM FOR RECORDING CALIBRATION DATA

ANALYZER MAKE AND MODEL _____

CODE NUMBER _____ SERIAL NUMBER _____

POLLUTANT _____ RANGE, ppmC _____

DATE OF CALIBRATION _____ OPERATOR _____

DERIVED CURVES _____

_____

Concentration, ppmC	Analyzer Response–DAS Voltage		
Unadjusted Data	NMOC	CH_4	TOC
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
Adjusted Data			
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____

TABLE 6. FORM FOR RECORDING ZERO AND SPAN DATA

ANALYZER MAKE AND MODEL _____

CODE NUMBER _____ SERIAL NUMBER _____

POLLUTANT _____ RANGE, ppmC _____

Date	Zero Response	Span Response	Span Concentration	Slope	Intercept

TABLE 7. FORM FOR RECORDING A ROUTINE MAINTENANCE SCHEDULE

ANALYZER MAKE AND MODEL: _____

SERIAL NUMBER: _____

Function	Frequency	Date Performed				

2.2.4 Setup

After generally understanding how the analyzer works, the operator is prepared to follow the manufacturer's instructions for setting up the unit. During the setup of any analyzer which uses hydrogen gas, carry out a leak check of the hydrogen flow system. (See section 2.4.2 for details in leak-checking flow systems.)

The hydrogen (H_2) gas for the FID requires extreme caution during handling due to its highly flammable nature. Colorless and odorless H_2 gas leaking into an unventilated area is very dangerous and is potentially explosive. The following precautions summarize safety considerations when using high pressure H_2 cylinders. Additional information on H_2 cylinder safety, as well as safety when using electrolytic hydrogen generators, is contained in reference 13.

1. Store H_2 cylinders in a secured, well ventilated, non-flammable area, preferably outdoors and out of direct sunlight. Secure the cylinder to a wall prior to installing the pressure regulator. Do not store H_2 cylinders beside cylinders containing corrosive or highly oxidizing materials.

2. The H_2 regulator should be dedicated to H_2 gas only. The output stage should contain a pressure relief valve. A flow restrictor must be connected to the exit of the regulator to limit gas flow in the event of a break in the H_2 tubing. If the output pressure of a new cylinder is less than the typical charge pressure (~ 2200 psig), leak-check the cylinder valve while at full clockwise and full counter-clockwise position.

3. Use only clean or new 3 mm (1/8 in) diameter stainless steel tubing to supply H_2 to the analyzer. Thoroughly leak-check the hydrogen line by pressurizing the line up to the analyzer. Turn off the H_2 cylinder valve and observe the outlet pressure. There should be no decay in pressure after 30 minutes. If there is a leak, pressurize the line and search for the leak using a liquid leak detector.

4. When ordering hydrogen cylinders, specify TOC concentration to be less than 0.1 ppmC.

5. A particulate filter (in a metal holder) can be located on the outlet of the regulator to ensure that no particulates enter the analyzer, and subsequently, the FID. Carefully leak-check each filter holder after the filter is changed.

After the hydrogen system is determined to be safe, recorder and gas connections can be made to the analyzer. A terminal strip for connecting recorder leads is usually located on the back of the analyzer. Follow instruction manual directions for identifying each channel and the voltage outputs from each. Care should be exercised by using signal cable that contains no splices and is as short as possible. Follow the recorder manufacturer's suggested procedures in installing the recorder. Signal cable should be connected to recorders and analyzers with approved connectors that are either soldered or crimped to the signal cable. Do not wrap bare cable around a connector.

Gas connections can now be made to the inlets located on the rear of the analyzer. All sample gas tubing should be composed of Teflon® and be connected to the analyzer and sample manifold with either stainless steel, Teflon®, or all glass connectors. Ensure that the tubing has not been previously used. Specific size tubing is addressed in the analyzer sections of this document. An all-Teflon® particulate filter, with a pore size of 5 microns or less, should be installed in the sample line. The sample line should be as short as possible, not exceeding 3m (10 ft.).

2.3 OPERATION

2.3.1 Start-up

> REMINDER: SECTION 2 IS INTENTIONALLY GENERAL. MORE SPECIFIC INFORMATION IS CONTAINED IN THE ANALYZER SECTIONS TO AID THE OPERATOR DURING START-UP.

By this time, the operator should have a basic understanding of the analyzer's operation, should be assured that the hydrogen flow system does not contain leaks, and should have a set of summary sheets which will aid in operating the analyzer. It is important to achieve these goals prior to starting up the analyzer because the complexity of the system may disguise malfunctions and lead the operator toward improper repairs or unsafe conditions.

After initial settings and adjustments are complete, supply power to the analyzer, allow the support gases to flow into the unit, and attempt to ignite the burners. Do not be concerned with flameouts during the first 15 minutes of operation. If after this period flameouts continue, allow the flame to extinguish. Allow the analyzer to warm up for twenty-four hours to ensure that heated elements are up to operating conditions and attempt ignition if the burner(s) is not already operating. If ignition difficulties persist, consult troubleshooting. While the analyzer is stabilizing, set up the recorder(s) as per the manufacturer's suggestions. Perform maintenance on the recorder to verify operation and ensure that the recorders will not be responsible for faulty data.

If the analyzer is new, the flow rates and pressure gauges should have already been correctly adjusted by the manufacturer. Do not adjust pressure gauges or flow controls if minor discrepancies exist between your readings and the Manufacturer's Final Data Sheet. Major discrepancies, such as no gas flow into the FID, should obviously be investigated. If the analyzer is not new, adjustments should be made to bring the flow rates and gauge settings into the ranges recommended in each analyzer section of this document or the instruction manual.

2.3.2 Periodic Calibrations And Zero/Span Checks

An initial multipoint calibration is recommended to establish the calibration curve and determine response linearity. Periodic zero and span checks are thereafter necessary to update the curve, with less frequent multipoint calibrations to verify response linearity. The frequency of zero and span checks and multipoint calibrations should be based on the analyzer's performance. Analyzer performance should be monitored using a control chart which documents analyzer response to standards, thus allowing calculation of response variation to standards. Section 2.0.9 of reference 10 contains additional information on calibration of automated analyzers. Appendix H of reference 14 discusses application of the control chart. Although these discussions are directed to analyzers that monitor ambient air for criteria pollutants, application of this strategy to NMOC anlayzers is recommended. Further details on calibrations are contained in section 3 and within each specific analyzer section.

2.3.3 Operational Checks

After the NMOC analyzer is calibrated and on-line, routine checks of operational parameters are recommended. These checks are part of the quality control program and include recording pressure gauge, rotameter, and pyrometer readings. The gauge and meter readings should be recorded immediately following a multipoint calibration and should be designated as the reference readings. Readings taken during subsequent checks should be compared to the reference readings to determine if operational parameters have shifted. (These data can be recorded on routine check sheets similar to Table 4. Specific forms for other analyzers are included in each analyzer section of this document.) The sensitive nature of NMOC analyzers requires investigations of any substantial drift in operational parameters. Assistance in such investigations is given in the troubleshooting sections of the instruction manual and this document.

2.3.4 Preventive Maintenance

The complex pneumatic systems and controls contained within NMOC analyzers necessitate thorough maintenance procedures and schedules. Adherence to the manufacturer's maintenance schedules is required to obtain reliable monitoring data. The importance of maintenance performed by experienced

personnel cannot be overemphasized. The manufacturer's instruction manual details procedures and schedules. Comments on areas of primary importance follow.

1. It is strongly recommended that maintenance of NMOC analyzers be performed by a competent, qualified person. This person should "specialize" in NMOC analyzer operation, maintenance, and repair and should be prepared to devote a substantial portion of time to such matters.

2. The hydrogen flow systems should be leak-checked during start-up and at least once every 180 days of operation. (A leak-check procedure is discussed in section 2.4.2.)

3. The analyzer's sample pump should be evaluated every 180 days of operation to ensure that it has the capacity to maintain necessary flows and pressures. (Sample pump evaluation is discussed in section 2.4.3.)

4. Check for loose or dusty electronic cards every 30 days of operation.

5. Check the particulate filter in the sample line at least every month and replace when it becomes visibly soiled.

6. Evaluate chromatograms weekly. Analyzers that contain chromatographic columns are usually designed to output chromatograms. A chromatogram is a valuable troubleshooting tool because it is a "fingerprint" of the analyzer's operation. A chromatogram should be obtained while the analyzer is sampling the methane and propane standards, so gate timing and sensitivity can be evaluated and compared to previous chromatograms. These evaluations can indicate a forthcoming malfunction. (The specific analyzer sections contain additional information on chromatograms.)

2.4 TROUBLESHOOTING

2.4.1 Flow Measurements

The sensitivity of NMOC analyzers requires proper flow rates throughout the analyzer. If pressure gauge readings of flow systems begin to decay, calibration curves begin to drift in one direction, or balance procedures cannot be performed, flow systems may be developing leaks or obstructions. When any of these potential problems cannot be corrected by adjusting pressure gauges to reference readings obtained during the last multipoint calibration, flow rates throughout the analyzer should be measured and compared to flow rates obtained during the last multipoint calibration. To

enable comparison, all flow rates must be corrected to standard temperature and pressure (25° and 760 mm Hg). Details on flow rate corrections are contained in section 2.1.2 of reference 10.

2.4.2 Leak-checks

If measurements indicate reduced flow rates, a leak or obstruction may be present in the flow system. This section discusses a leak-check procedure and identifies apparatus that can aid in verifying or locating a leak. The test apparatus addressed can be fabricated from materials readily available to most monitoring programs; however, it may not be as sensitive as a leak-check device produced by the analyzer manufacturer.

> CAUTION: INDISCRIMINATE APPLICATION OF LEAK DETECTOR SOLUTIONS CAN BE HARMFUL TO ELECTRONIC COMPONENTS. SINCE LOW FLOW RATES IN NMOC ANALYZERS REDUCE THE EFFECTIVENESS OF SUCH SOLUTIONS, THE USE OF LEAK DETECTOR SOLUTIONS IS RECOMMENDED ONLY UNDER SPECIAL CIRCUMSTANCES, AS DETAILED LATER IN THIS SECTION.

1. Locate all gauges and flow systems on the instruction manual's flow chart and highlight each system with different colors. (Red for H_2, green for carrier, etc.)

2. Construct a leak-check apparatus as shown in Figure 1 using a pressure source (compressed air or nitrogen containing < 0.1 ppmC TOC), pressure regulator, toggle valve, a 340 kPa (50 psig) pressure gauge graduated in 7 kPa (1 psig) increments, flexible tubing, and an exit cap.

3. Leak-check the apparatus by applying pressure, closing the toggle valve, disconnecting the pressure source, and observing the pressure gauge reading for 30 minutes. If there is no decay in the pressure reading, the apparatus contains no leaks. If a leak develops, locate it with a liquid leak detector and repair it. Recheck for leaks.

4. Connect the leak-check apparatus to the inlet of the analyzer's flow system to be leak-checked (either a span gas inlet, carrier gas inlet, support air inlet, hydrogen gas inlet, or sample inlet). Ensure that the sample pump is not in the system to be checked. If it is, bypass it with tubing.

5. Cap the exit(s) of the system to be leak-checked. Most systems exit into the FID; therefore, locate the flow system's last fitting from the FID and connect the exit cap. AVOID TOUCHING THE THREADS OF THE FID AND FITTING.

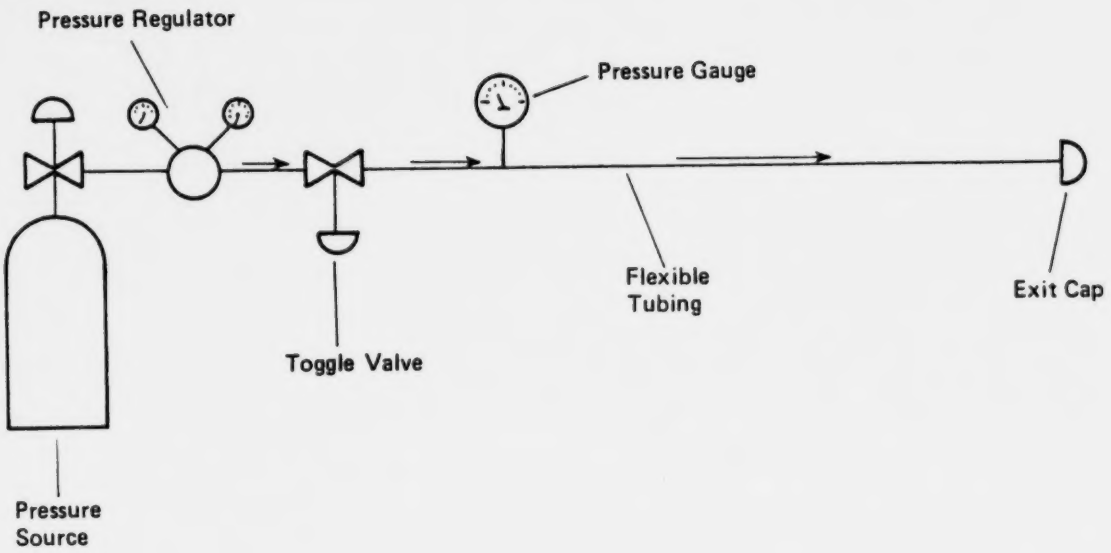

Figure 1. Leak-check apparatus.

6. Apply a pressure level to the flow system which will not exceed maximum allowable pressures in the analyzer and close the toggle valve on the apparatus. The instruction manual or pressure gauge in-line will indicate maximum allowable pressures.

7. Monitor the pressure gauge located on the apparatus. If after 30 minutes there is no decrease in the pressure reading, the flow system contains no leaks. If pressure decrease occurs, relocate the apparatus and pressurize one-half of the analyzer's flow system. Continue moving the apparatus until a general area of the flow system containing the leak is identified. Carefully apply the leak detector solution to the fittings and tubing if necessary. Foaming or bubbles indicate the location of the leak. Inspect the fitting or valve and replace or repair as necessary.

8. After repairing the leak, recheck the entire system to verify that all fittings or valves are functioning properly with no leaks.

2.4.3 Sample Pump Checks

Once every 180 days of operation, determine if the sample pump can supply the necessary head pressure recommended in the manufacturer's instruction manual. Perform the check by connecting a high pressure gauge to the outlet of the pump and capping the exit from the gauge. Start the pump and record maximum pressure output. A noticeable decrease in head pressure from the last sample pump check may indicate that the pump needs service.

SECTION 3

CALIBRATION STANDARDS, EQUIPMENT, AND PROCEDURES

3.1 INTRODUCTION

As noted in other sections of this TAD, the response of an FID analyzer may vary considerably from one organic compound to another. Thus, the choice of the calibration species has a direct bearing on resulting analyzer calibration. Historically, continuous ambient NMOC analyzers have been calibrated largely with methane-in-air standards. Methane was used primarily because it is chemically simple (C=1, and ppmC = ppmV), it is readily available, and it can be used to calibrate both CH_4 and TOC measurement channels (from which NMOC measurements are derived by subtraction).

But propane-in-air standards have also been used to calibrate automated NMOC analyzers because (the contention is) propane allows a more accurate measurement of the NMOC concentration in ambient air. This contention is supported by the following facts and reasons:

1. Propane is more representative (than methane) of the hydrocarbon mix used to calibrate hydrocarbon analyzers that collected the data base from which the EKMA model was developed.

2. In a recent study (9), automated NMOC analyzers measured individual NMOC compounds commonly found in ambient air. Response to propane was found to be approximately equal to the average response to all compounds measured. Response to methane was found to be 20 to 30% greater than the average response to all compounds measured.

3. In a recent study (9), analysis of ambient air by automated NMOC analyzers calibrated to propane produced responses that agreed quite well with sum-of-species GC-FID results. Agreement between these methods was also quite good when sampling synthetic organic mixtures.

4. Direct reading, automated NMOC analyzers (that do not produce CH_4 or TOC output) are generally calibrated to propane standards (they obviously would not respond to methane standards).

For these reasons, EPA recommends that continuous NMOC data, obtained for use in dispersion models for predicting ozone concentrations, should be referenced to propane standards. CH_4 and TOC responses should be balanced and referenced to methane standards. Discussions on calibrations and standards are contained in this section.

3.2 ZERO AIR STANDARDS

The first step in calibrating an NMOC analyzer is to obtain the response to a hydrocarbon-free matrix. Ideally, this matrix should approximate "clean" ambient air; that is, air containing only nitrogen, oxygen, carbon dioxide, and water vapor. Since the analyzer's response to this matrix is its baseline or "zero" response, the matrix is frequently referred to as "zero air".

Zero air is actually not totally free of all organic (or other) compounds, but is usually considered adequate if the TOC concentration is less than 0.1 ppmC. It is important that zero air contain ambient quantities of oxygen, but carbon dioxide and water vapor may also be present. The effects of oxygen content variations have been studied (9) and determined to have a significant effect on FID response. Moisture and carbon dioxide effects on FID response are not as well understood; therefore, the recommended zero air standard should contain 20.9 $\pm$ 0.3% oxygen in a nitrogen balance with TOC concentration <0.1 ppmC.

The recommended method for preparing zero air is by scrubbing and oxidizing unwanted compounds from ambient air. Such cleanup systems are usually large and contained in the laboratory but may also be small and contained in the analyzer itself. Zero air is also available from specialty gas manufacturers who compress the air and store it in cylinders; however, this source of zero air is not recommended due to possible variable oxygen concentrations, economic considerations, and frequent bottle changes.

A typical cleanup system recommended for producing zero air for NMOC analyzers is shown in Figure 2. Ambient air should be drawn from the outside of the building and filtered before being compressed. Use of outside air is more likely to provide true ambient concentrations of oxygen and nitrogen in the zero air matrix. The dryer removes moisture before the air enters the scrubber unit. As the air passes through the scrubber unit, compounds such as nitrogen dioxide (NO_2), sulfur dioxide (SO_2), ozone (O_3), etc., are removed. The air then enters the heated catalytic oxidizer where organics and carbon monoxide (CO) are converted into carbon dioxide (CO_2) and water (H_2O). Since many laboratories prepare zero air, different detailed designs are acceptable if the resulting product is determined to be within the specifications previously mentioned. (Note: All pressure regulators should be LOX cleaned and contain non-permeable, metal diaphragms. Do not use a heatless air dryer in the zero air system because it will alter oxygen levels in the sample.)

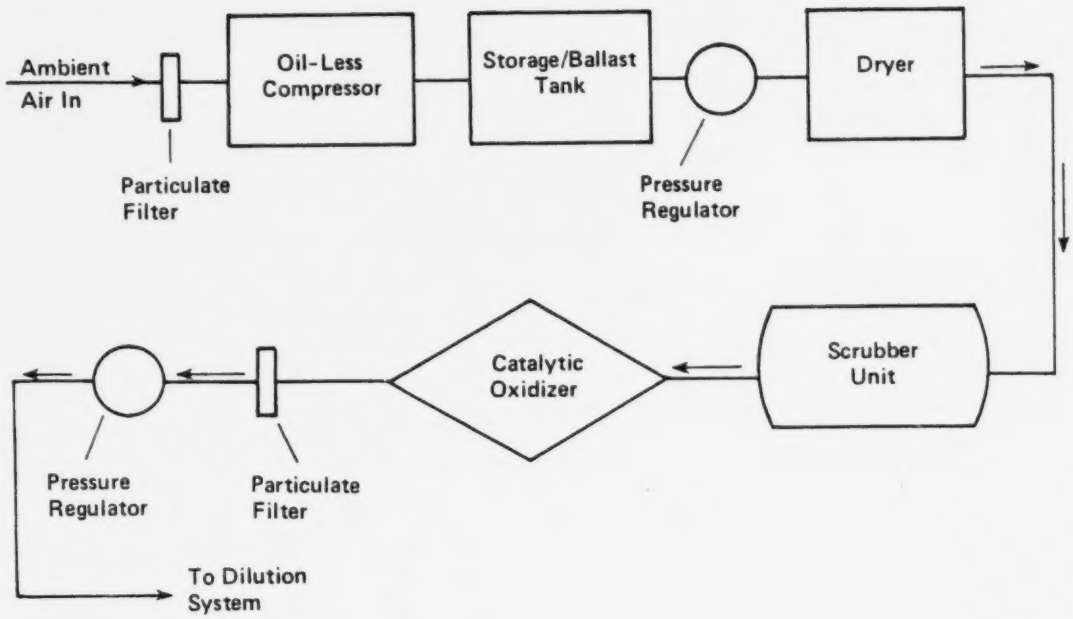

Figure 2. Diagram of a zero air system.

Cleanup systems contained within NMOC analyzers may use only a heated catalyst to oxidize organics. Care should be taken to ensure that the heater and catalyst are properly maintained. This internal system should be used only for level 2 zero checks (section 3.9) unless it has been verified against an external cleanup system. Many monitoring sites normally contain an external zero air system so a common zero matrix can be delivered to all analyzers at once.

As mentioned before, zero air compressed in cylinders can also be utilized to zero the analyzer, although this is not recommended. If compressed gas is used, ensure that it has the correct oxygen content and that it is delivered to the analyzer's inlet at atmospheric pressure. Failure to supply a vent between the cylinder and the analyzer will pressurize the sample system and could result in improper flows or damage to internal flow controls. (See the discussion on calibration gas dilution systems in section 3.5.)

3.3 SPAN GAS STANDARDS

As noted earlier, both methane and propane standards are required to calibrate an automated analyzer that produces CH_4, TOC and NMOC outputs. These standards are available from several commercial manufacturers in

compressed gas cylinders at a variety of concentrations. Standards must be traceable to a Standard Reference Material (SRM) from the National Bureau of Standards (NBS) or to a commercially certified reference material (CRM). The procedure to certify a cylinder of gas as traceable to an NBS/SRM or CRM can be performed by the gas manufacturer or the user. (Traceablity protocol is addressed in reference 15 or in section 2.0.7 of reference 10.) Table 8 lists several concentrations of methane and propane SRM's that are available from NBS; however, only one SRM is required for traceability purposes. Reference 16 addresses NBS/SRM's; consult gas manufacturers about the availability of CRM's. Methane and propane standards can be combined in a single cylinder with an ambient air balance. Such a gas cylinder containing both standards may be used for spot checks between calibrations, but will not permit the CH_4 and TOC channels to be balanced.

Inconsistent results from NMOC analyzers have been partly attributed to contaminated calibration standards. For this reason, the methane and propane standards should not only be referenced to an NBS/SRM or CRM every three to six months, but they should also be analyzed yearly to ensure that the concentrations of organic contaminants remain less than 0.1 ppmC. For example, the methane standard should contain less than 0.1 ppmC NMOC, and the propane standard should contain less than 0.1 ppmC organics other than propane. Both standards must contain ambient levels of oxygen in a nitrogen background if no ambient level diluent air is to be blended with the standards.

TABLE 8. LISTING OF METHANE AND PROPANE NBS/SRMs AVAILABLE IN COMPRESSED GAS CYLINDERS

SRM	GAS	ppmV	ppmC
1658A	CH_4/Air	0.951	0.951
1659A	CH_4/Air	9.43	9.43
1660A	CH_4/C_3H_8/Air	4.10 (CH_4), 0.976 (C_3H_8)	4.10 (CH_4), 2.928 (C_3H_8)
1665	C_3H_8/Air	3	9
1666	C_3H_8/Air	10	30
1667	C_3H_8/Air	50	150
1668	C_3H_8/Air	100	300
1669	C_3H_8/Air	500	1500

3.4 EFFECTS OF MOISTURE

The effects of moisture on automated NMOC analyzers is not well known. Recommendations are therefore not available. Preliminary investigations indicate that analyzers addressed in this document will not be affected by moisture if the precautions in each analyzer section are followed.

3.5 CALIBRATION GAS DILUTION SYSTEM

There are basically two methods to deliver calibration standards to automated analyzers in the field: by dynamic dilution of a single high concentration standard with zero air, and by using compressed gas cylinders containing calibration concentrations. The dynamic dilution approach is recommended for calibrating automated NMOC analyzers because this approach offers greater stability of the high concentration standard in a cylinder, greater control of oxygen content in the sample, greater ease in delivering a variety of accurate calibration standards, and a lower cost to produce different concentration levels. However, accurate flow measurements are required.

A dynamic dilution system, as shown in Figure 3, can be used to dilute a high concentration standard with zero air. This system requires flow controllers or needle valves to control diluent and pollutant flows; a flow meter to measure the flow rates; stainless steel, Teflon®, or glass tubing to direct the flows; a glass mixing flask to blend the two flows; and a glass manifold or tee for sampling the standards. The manifold must be vented to the atmosphere to prevent pressure buildup in the sample line connected to the analyzer's SAMPLE port (not CALIBRATE port)! To prevent contamination of the calibration standard by the room atmosphere, all unused sample ports on the manifold must be sealed, and the flow to the manifold must be 20 to 50% greater than the analyzer's sample demand. To maintain oxygen at 20.9 ± 0.3%, the diluent to pollutant flow rate ratio should be greater than $\overline{100}$:1.

Care must be taken to ensure that the system contains no leaks that can introduce error into flow measurements or allow contaminants to enter the system. Leaks may be detected by applying a low level of pressure to the system and submerging the glassware and tubing in a bath, or by using a liquid leak detector on the fittings. Care must also be taken to ensure that the system is clean and maintained to prevent contamination. Use only new tubing and glassware to construct a dilution system.

3.6 FLOW MEASUREMENTS

Preparing a known pollutant concentration by dynamic dilution requires accurate measurement of both pollutant and diluent flow rates. Flow rates must be corrected to standard temperature and pressure (25°C and 760 mm Hg) unless two measurements taken with the same flowmeter are to be ratioed. For

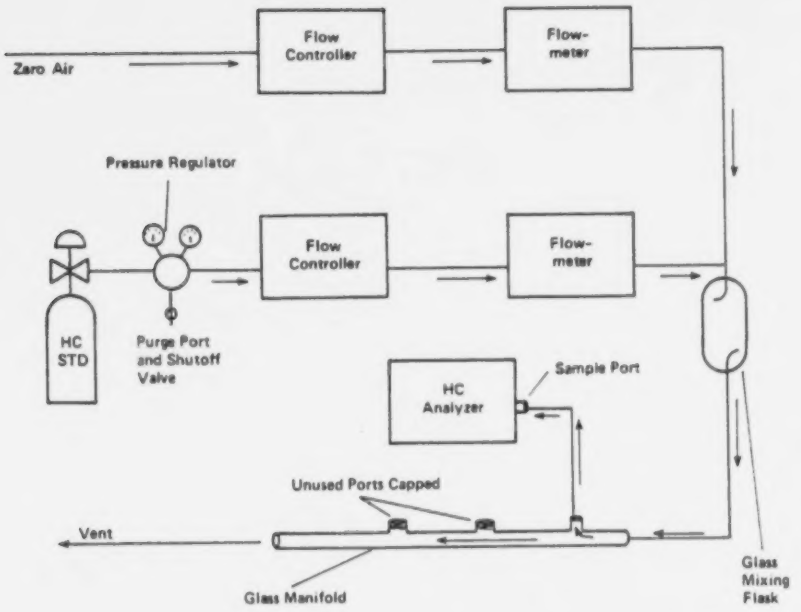

Figure 3. Diagram of a dilution system.

corrections, atmospheric pressure and temperature in the flow measurement area must also be measured. The flow measurement device must be traceable to an NBS standard. Two devices commonly used to measure flows in the field are soap bubble flowmeters (SBFM) and wet test meters (WTM). Details on calibrating flow measurement devices are given in section 2.1.2 of reference 10. Comments concerning areas of specific concern follow.

1. When using an SBFM, select a bubble tower that will permit a flow measurement for at least 15 seconds. That is, use a 10-cm^3 tower for flow rates less than 40 cm^3/min, use a 100-cm^3 tower for flow rates between 40 and 400 cm^3/min and use a 1000-cm^3 tower for flow rates between 400 and 4000 cm^3/min.

2. During SBFM measurements, allow only one bubble to traverse the column while measuring the time interval. The entire calibrated portion of the column should be used during the measurement. If the bubble bursts before it traverses the column, check to see if the column is clean (clean regularly with hot, soapy water and rinse well) and is not in hot or cold drafts. A standard soap solution designed for flow measurements can reduce the difficulties with bubble flows.

3. Wet test meters should generally be used within a flow range of 1/3 to 3 meter revolutions per minute. A one liter per revolution WTM, for example, should be used within the range of 1/3 to 3 liters per minute. WTM's are available in many different capacities, covering a wide range of applicable flows.

4. WTM calibration factors vary with the flow rate through the meter. When WTM's are used to measure dynamic flows (rather than incremental volumes), the ideal calibration (capable of 1% accuracy) should relate measured flow rate to actual flow rate (both adjusted to some common set of reference conditions). However, if meters using factors are operated within the range of 1/3 to 3 revolutions per minute, an accuracy of 2 to 3% can be expected.

5. Flows through WTM's should be measured by complete meter revolutions only. Additionally, the number of timed, complete revolutions should be chosen so the timed interval is not less than 20 seconds.

3.7 GENERAL MULTIPOINT CALIBRATION PROCEDURE

The actual procedure by which an NMOC analyzer calibration is referenced to propane varies, depending on the design of the analyzer, and specifically, the number and type of output channels, the number of zero and span controls available, and whether the TOC-CH_4 subtraction is implemented on signals before or after they are processed by the span control circuits.

The following generalized procedure illustrates the normal sequence of steps that are recommended for calibrating an NMOC analyzer. This general procedure must be individually adapted to the particular design of each NMOC analyzer. For example, in its normal configuration, the MSA Model 11-2 analyzer has no TOC output channel. Therefore the internal TOC reading necessary to obtain the NMOC reading must be balanced to the CH_4 channel to provide a zero NMOC reading when sampling methane. More explicit information on the exact calibration procedure for each analyzer is contained in the analyzer-specific sections of the TAD and in the operation manual for each analyzer.

1. Sample zero air and adjust all channels to read 0.0 ppmC.

2. Sample a concentration of the methane standard equivalent to about 85% of full scale. Adjust the span controls of both the CH_4 and the TOC channels' outputs. Make sure the TOC response equals the CH_4 response so that subtraction of the CH_4 response from the TOC response will yield an NMOC response of 0.0 ppmC. (This balance may be accomplished in certain models by adjusting the

hydrogen or sample flow rate to the FID. Analyzers without a TOC output must be balanced to ensure that the NMOC reads 0.0 ppmC.) If substantial adjustments are necessary, resample zero air and adjust the zero responses as necessary, then repeat the balance.

3. Sample at least two additional concentrations of the methane standard approximately equally spaced over the scale range. Record the CH_4 and TOC responses. Least squares regression of the analyzer responses (dependent variable, Y) against the calibration concentration (independent variable, X) should result in a correlation coefficient of 0.9996 or better if the channel is linear.

4. Sample a concentration of the propane standard equivalent to about 85% of full scale. The CH_4 channel's response should equal zero. Analyzers with an independent NMOC channel span pot may be adjusted as necessary to make the NMOC channel's response equal to the propane concentration. Do not adjust the TOC channel's response. If substantial adjustments are necessary, resample the zero standard and the methane standard as before.

5. Sample at least two additional concentrations of the propane standard approximately equally spaced over the scale range, and record the NMOC response. Least squares regression, as before, should result in a correlation coefficient of 0.9996 or better if each channel is linear.

NOTE: WHEN THE NMOC CHANNEL IS CALIBRATED WITH PROPANE, THE SUM OF THE CH_4 AND NMOC CONCENTRATIONS MEASURED WILL NOT EQUAL THE MEASURED TOC CONCENTRATION BECAUSE OF THE DIFFERENCE IN FID RESPONSE BETWEEN METHANE AND PROPANE.

After linearity is established, generate the regression equations that define the curves for each channel and post the calibration curve, date, and channel identification on the appropriate recorder. All calibration data and curves can be entered on a form similar to Table 5 and filed in the calibration section of the analyzer's log book. See section 2.0.9.1.2 of reference 10 for more detail on calibration theory.

For analyzers which have no direct NMOC output, calculate NMOC response using the following equation:

$$\text{NMOC response} = \left(\frac{\text{TOC response to sample} - \text{TOC response to zero}}{\text{TOC slope to methane}} - \frac{\text{CH}_4\text{ response to sample} - \text{CH}_4\text{ response to zero}}{\text{CH}_4\text{ slope to methane}} \right) \frac{\text{TOC slope to methane}}{\text{TOC slope to propane}} \quad (1)$$

An example calculation using actual calibration curves and ambient data responses from an NMOC analyzer follows.

Methane calibration curves
CH_4 response = 9.658X + 0.2256
TOC response = 9.731X - 0.0359

Propane calibration curves
TOC response = 6.536X + 0.111

Analyzer responses to ambient air following calibration
CH_4 channel = 22.1% Chart
TOC channel = 41.9% Chart

Applying the data to the NMOC equation:

$$\text{NMOC response} = \frac{41.9 + .0359}{9.731} - \frac{22.1 - .2256}{9.658}\ \frac{9.731}{6.536} = 3.04 \text{ ppmC} \qquad (2)$$

3.8 LEVEL 1 ZERO AND SPAN CHECK

The purpose of the level 1 zero and span check (see section 2.0.9 of reference 10) is to periodically correct the most recent calibration curve for zero and span drift. Once linearity is established in a multipoint calibration, the calibration needs to be checked with only two points; usually at zero and 85% full scale. The standards and the procedure used during the multipoint calibration should be used, except that during the level 1 check, only one upscale concentration is necessary.

All NMOC measurements obtained from the analyzer should be converted to ppmC via the most recent calibration curve or zero and span check. Accordingly, adjustments to the zero and span pots need be made only if considerable drift has occurred. (See section 2.0.9.1.3 of reference 10 for details on drift.) For example, Phase II of the EPA's Equivalency Designation Program specifies that zero adjustments of analyzers are needed if the zero response drifts more than $\pm$ 3% of full scale from the intercept of the most recent multipoint calibration curve. Span adjustments are to be made only if the slope of the new calibration curve drifts approximately more than $\pm$7% from the slope of the most recent multipoint curve.

To calculate zero drift on an NMOC analyzer operating in the 0 to 10 ppmC range, subtract the level 1 zero response from the intercept of the most recent multipoint curve. (Response and intercept must be in the same units.) The difference is the zero drift, which should be greater than $\pm$0.3 ppmC, or $\pm$3.0% full scale, to warrant a zero pot adjustment.

To calculate span drift, first determine the slope of the Level 1 calibration curve using the equation:

$$\text{Slope of level 1 calibration curve} = \frac{\text{Level 1 span response - Level 1 zero response}}{\text{Level 1 span concentration}} \quad (3)$$

(Be sure to report response and concentration in units identical to those used in the multipoint calibration curve.) Calculate span drift using the equation:

$$\% \text{ span drift} = \frac{\text{Slope of level 1 calibration curve} - \text{Slope of multipoint calibration curve}}{\text{Slope of multipoint calibration curve}} \times 100 \quad (4)$$

The drift should be greater than about $\pm 7\%$ to warrant a span pot adjustment. (See section 2.0.9.1.3 of reference 10 for more details.)

NOTE: BEFORE POTENTIOMETERS ARE ADJUSTED, CHECK ALL OPERATIONAL PARAMETER READINGS AND ADJUST THOSE THAT HAVE DRIFTED FROM READINGS TAKEN AFTER THE LAST MULTIPOINT CALIBRATION. NMOC ANALYZERS ARE VERY SENSITIVE TO CHANGES IN OPERATIONAL PARAMETERS (FLOW RATES, ETC).

3.9 LEVEL 2 ZERO AND SPAN CHECK

A level 2 zero and span check may be used between the regular level 1 zero and span checks as an unofficial test of analyzer response. This level 2 check may use non-traceable or uncertified standards which may enter the analyzer at a point other than the normal sample inlet (e.g., span inlet). No adjustments are made to the analyzer based on a level 2 check, which is primarily a check of repeatability and operation rather than of absolute response. If used, the level 2 check should be carried out immediately following a regular level 1 check or multipoint calibration to obtain reference readings. At subsequent checks, if the readings have changed appreciably, then a level 1 zero and span check or a multipoint calibration should be carried out to determine if the analyzer requires adjustment. (See section 2.0.9.1.3 of reference 10 for more details.)

SECTION 4

AUGMENTED PROCEDURES FOR THE MSA 11-2
CONTINUOUS NMOC/METHANE MONITOR

NOTE - READING SECTIONS 1, 2 AND 3 BEFORE SECTION 4 IS STRONGLY RECOMMENDED. INFORMATION WHICH IS CRITICAL TO THE UNDERSTANDING AND SUBSEQUENT ACCURATE OPERATION OF THIS ANALYZER IS DETAILED IN THOSE SECTIONS AND WILL NOT BE REPEATED HERE.

4.1 PRINCIPLES OF OPERATION

The MSA 11-2 continuously splits an ambient sample into two aliquots for passage into separate FIDs. One aliquot is directed to FID #1 where TOC concentration is measured, and the second aliquot is directed through a heated cutter (Hopcalite® is used to oxidize all hydrocarbons other than methane to CO_2 and H_2O) prior to entering FID #2, where the methane concentration is measured. The CH_4 response is then electronically subtracted from the TOC response to produce the NMOC response. The NMOC and CH_4 responses are then directed to the recorder outputs.

4.2 SYSTEM DESCRIPTION

A description of the analyzer with photographs is given in the analyzer's instruction manual. To avoid redundancy, this text will not address location of components, but rather, emphasize precautions when using critical components.

4.2.1 Flame Ionization Detectors

The analyzer contains two FIDs that enable monitoring NMOC and CH_4 concentrations simultaneously. The response from the two FIDs must be balanced to a methane-in-air standard.

4.2.2 Hydrogen Pressure Gauges

The flow of hydrogen fuel to each FID is controlled by a separate pressure regulator, gauge, and restrictor. Increasing the pressure reading on

the hydrogen gauge will increase the flow of hydrogen to the burner and affect the sensitivity of that FID.

4.2.3 Ignitor Switches (Flame-out Indicators)

Two push button controls located on the front panel control the flow of hydrogen to each FID. When the button is depressed, hydrogen will flow to the FID then ignite. When the FID ignites, the light in the button will turn off. During subsequent flameouts, a solenoid will shut off hydrogen flow and the light in the button will turn on. The flameout indicator is controlled by a thermistor located above the flame in the FID. If the sensitivity of the thermistor is not properly adjusted, the light in the button may not show true flame status (i.e., the indicator may be off while the flame is out). Adjustments can be made on the Dual Flame-Out Card to correct this condition. If the status of the flame is in doubt, observe analyzer response first to zero air and then to a sample known to contain methane. If the CH_4 channel's responses are the same to both samples, the CH_4 channel's flame is out. If the response varies, the flame is burning. Check the NMOC channel's flame status with zero air and a sample known to contain NMOCs (propane).

4.2.4 Air Pressure Gauge

Burner airflow rate, condensate trap vent flow rate, sample vent flow rate, and sample flow rate to the FID are all related to the air pressure gauge reading on the front panel. Variations in this reading indicate a potential malfunction which requires troubleshooting (section 4.7.1.).

4.2.5 Back-Pressure Regulator

Located in the oven are two non-adjustable back-pressure regulators (one in older models) that control sample flows to the FIDs by controlling the pressure applied to the two sample capillaries. The pressure gauges connected to these regulators and the flow rates that vent from the regulators should be checked regularly because variations in these parameters indicate a potential malfunction that requires troubleshooting (section 4.7.1).

4.2.6 Heated Oven

The FID burners, associated electronics, and pneumatics are contained in a heated oven maintained at 50 to 55° C. Small fluctuations in the room temperature therefore do not affect these critical components. Opening the oven door will obviously cause a loss of heat that may affect the analyzer response; therefore, it is good practice to perform measurements and adjustments on equipment located inside the oven several hours prior to a multi-

point calibration or level 1 zero and span check. If opening the oven door is necessary, close it as soon as possible to minimize the thermal upset.

4.2.7 Oxidizer

The oxidizer contains palladium and Hopcalite® heated to between 340 to 350° C. At this temperature, all hydrocarbons and carbon monoxide are removed, leaving a source of hydrocarbon-free air. This air is primarily used for burner air in the FIDs but can also be tapped and delivered to the FIDs as a zero air standard.

The use of oxidizer air as a zero air standard is not recommended during multipoint calibrations or level 1 zero and span checks if an external zero air source is used to dilute the span gas standard. Oxidizer air can be used in level 2 zero and span checks.

4.2.8 Cutter

The cutter contains MSA brand Hopcalite® that is heated to between 240 and 260° C. At this temperature, all hydrocarbons except methane are oxidized, allowing CH_4 to pass to FID #2. Use only MSA brand Hopcalite® if the catalyst ever requires replacement. Other catalysts may not perform properly at the temperature attainable by the cutter. (See section 4.7.1.8 for adjustments.)

4.2.9 Sample Filter/Moisture Trap

Compression of sample air by the analyzer pump almost always results in moisture condensation in the compressed sample air. It is imperative that none of this liquid water be allowed to pass into the analyzer. Liquid water entering the analyzer may damage the cutter or oxidizer, may result in clogged capillaries or orifices, and may damage other flow control components.

On the rear of older analyzers is a single Balston condensate trap for removing water from the sampler. This water removal system should be upgraded because it is susceptible to malfunction. Analyzers with this system may have been damaged by water during previous operation and should therefore be carefully inspected for damage in the cutter, oxidizer, FID, and connecting tubing.

On the rear of new analyzers is a water removal system consisting of two Balston filters and accessories. This system provides much greater protection against water entry into the analyzer and is discussed in detail in section 4.3.2.

4.3 MODIFICATIONS

4.3.1 Introduction

The original MSA 11-2 T/HC/Methane monitor was manufactured during the early 1970s to analyze ambient air continuously for CH_4, TOC, and NMOC concentrations. Modifications to the original design have occurred over the years, and an updated model called the MSA 11-2 Continuous NMOC/Methane Monitor is now available. The principles of operation and detection have not changed from the earlier model, but the following modifications have been made:

1. A more powerful sample pump manufactured by Air Dimensions Incorporated has replaced the smaller Thomas pump.

2. The pump is no longer mounted on the analyzer chassis.

3. A 10-micron Hoke particulate filter has been added to the exit of the oxidizer.

4. The moisture drop-out trap has been modified.

5. An activated charcoal filter has been added to the inlet of the cutter.

6. Electronic balance adjustments have been added to enable balancing the responses from the FIDs more closely.

7. The range change card has been modified to allow for ranges of 10 or 20 ppmC full scale.

8. The oxidizer volume has been increased.

9. The cutter has been moved from the interior of the oven to the rear of the analyzer chassis.

10. A back-pressure regulator and gauge have been added to the TOC sample line.

11. A modification has been made to the zero pot to enable zero offset to observe negative zero drift.

Modifications 1 through 6 should be made to older model 11-2 analyzers to obtain adequate NMOC data. The remaining modifications are less critical and may not be needed. The manufacturer suggests employing a factory-trained serviceperson to update the unit if the operator is not very familiar with this work.

4.3.2 Moisture Trap

It is imperative that no liquid water be allowed to enter the analyzer. For maximum protection against liquid water, using a trap system as shown in Figure 4 is strongly recommended. The filter (5 micron) removes particulates from the sample air and helps to avoid clogging of subsequent flow control components. The first condensate trap, consisting of a collection bowl, Balston filter, and drain valve, collects most of the liquid water. The valve is normally closed, but is manually opened to drain the water before the trap fills and water is drawn over to the second trap. In draining this trap, a small amount of liquid water should be left in the trap to humidify dry calibration gases during calibration or zero/span checks. Under conditions of high ambient humidity, the trap may fill in only a day or two and must be watched closely and drained frequently. More convenient operation can be obtained by replacing this first Balston trap with an automatic trap such as the Wilkerson M20-02-000 or equivalent. The Wilkerson trap has a built-in float valve that drains the trap automatically as needed, but always retains some liquid water in the trap.

The second water trap consists of a collection bowl, Balston filter, and a vent controlled by a back-pressure regulator. This trap provides secondary protection and collects any water carryover from the first trap. The continuous vent flow prevents any water buildup in this trap, which should never show more than a partial fogging.

Beyond the second trap is a valve which expands the sample air (by about 4 psig), thereby lowering its dew point and avoiding any subsequent condensation. This valve and its connection to the trap should rise vertically from the trap to discourage water droplets from approaching the valve. Finally, a section of transparent tubing (a rotameter with no ball works fine) follows the valve. This tubing provides a final verification that no liquid moisture is entering the analyzer. Any sign of condensation or fogging in this area indicates a malfunction in the trap system. See section 4.5.4 for procedures to set up and adjust the system and see 4.7 for troubleshooting procedures.

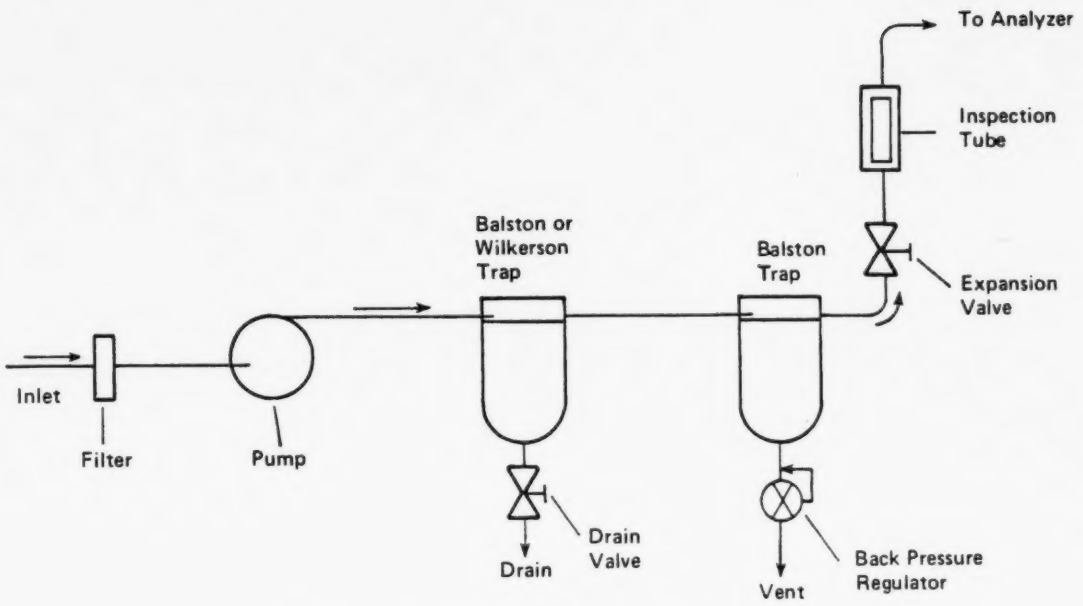

Figure 4. Recommended water trap system.

4.4 INSTALLATION

The manufacturer's instruction manual addresses procedures to install the analyzer. Additional comments follow.

1. Before supplying power to the analyzer, ensure that all electronic component cards are properly seated by attempting to push the cards snugly into the connectors. Be particularly certain that the electrometer box located inside the oven is properly seated.

2. Minimize the distance between the analyzer and the sample manifold. Use clean, 3 mm (1/8 in) diameter inert tubing to make the sample line. The sample line length should not exceed 3 m (10 ft).

3. Leak-checks should be made on the hydrogen flow system of old and new analyzers. The leak-check procedure outlined in section 2.4.2 can be used.

CAUTION: ONLY EXPERIENCED, QUALIFIED OPERATORS SHOULD PERFORM THE LEAK-CHECK. AVOID FINGER CONTACT WITH THE FITTING THREADS DUE TO POSSIBLE TRANSFER OF OILS THAT WILL TEMPORARILY INCREASE THE BASELINE RESPONSE.

4.5 OPERATION

4.5.1 Start-up

The MSA 11-2 analyzer has two selectable modes of operation. Channel 2 can be operated to output either TOC (non-subtracting) or NMOC (subtracting), depending on the location of a jumper on the electrometer card (see MSA Instruction Manual). For most NMOC monitoring applications, the NMOC mode is much more advantageous than the TOC mode; therefore, the NMOC (subtracting) mode is strongly recommended. Calibration and zero and span procedures in this TAD address only the CH_4/NMOC mode of operation. The NMOC mode is selected by placing the jumper in the "S" position.

With the ON/OFF switch in the OFF position, plug the analyzer's power cord into a power source that has been determined to be stable (see section 2.1.2 for details). Turn the switch to ON, light the FID burners, and monitor oxidizer, cutter, and oven temperatures. If temperatures do not rise, or if they rise beyond suggested levels, turn the analyzer off and consult troubleshooting procedures. If the temperature rises smoothly, allow the analyzer to warm up for 24 hours before recording the readings from the pyrometer and pressure gauges. With new analyzers, compare pyrometer and pressure gauge data to those supplied on the Manufacturer's Final Data Sheet. If disagreements exist, notify the manufacturer and ascertain if the difference is significant. If the analyzer has been used before, adjust flows, temperatures, and pressures to the values used previously. If previous settings are unknown, select trial settings within the ranges specified in Table 9. Flow measurement details and other procedures for setting up or checking out component operation are discussed in this section.

4.5.2 Periodic Calibrations and Zero/Span Checks

An initial multipoint calibration is recommended to verify linearity in the calibration curve, and periodic level 1 zero and span checks are thereafter necessary to update this curve. The frequency of level 1 zero/span checks and subsequent multipoint calibrations should be based on the analyzer's performance. Performance can be monitored through use of a control chart which documents responses to standards and ultimately enables calculation of variation in response to standards (drift). (See section 2.0.9 of reference 10 for details on calibration and level 1 and level 2 zero and span checks. See section H of reference 14 for details on control charts. See section 4.6 of this TAD for specific calibration procedures.)

TABLE 9. NOMINAL OPERATING SPECIFICATIONS FOR THE MSA 11-2 ANALYZER

Parameter	Specifications
Front Panel	
H_2 pressure reading (per gauge):	~~48~~ 34 to 62 kPa (~~7~~ 5 to 9 psig)
Air pressure reading:	138 to 152 kPa (20 to 22 psig)
Oven temperature:	50 to 55° C (122 to 131° F)
Oxidizer temperature:	340 to 350° C (644 to 662° F)
Cutter temperature:	240 to 260° C (464 to 500° F)
Oven	
Back-pressure regulator gauge(s) reading:	17 to 21 kPa (2.5 to 3.0 psig)
Back-pressure regulator vent flow rate:	500 ± 100 cm^3/min
Sample flow rate to FID No. 1:	12 to 14 cm^3/min
Sample flow rate to FID No. 2:	Equal to sample flow rate to FID No. 1
H_2 flow rate to FID No. 1:	15 to 20 cm^3/min
H_2 flow rate to FID No. 2:	~ Equal to H_2 flow rate to FID No. 1
Burner air flow rate to FID No. 1:	200 ± 50 cm^3/min
Burner air flow rate to FID No. 2:	200 ± 50 cm^3/min
Back Panel	
Moisture trap flow rates:	Set up and adjust as per section 4.5.4.

4.5.3 Operational Checks

The first six parameters listed on Table 9 should be checked at least once a week and more frequently if necessary. These readings, along with analyzer responses, zero and span pot settings, and other routine checks that may be necessary can be recorded on Table 10. (Routine monitoring may not require that unadjusted responses to standards be recorded; however, special cases may warrant such data.) If any of these parameters shows substantial change from the last check, or if drift out of the specified range has occurred, recheck the analyzer calibration with a level 1 zero and span check and make the necessary adjustments.

NOTE: FREQUENTLY CHECK THE MOISTURE TRAP FOR PROPER OPERATION DURING PERIODS OF HIGH RELATIVE HUMIDITY.

4.5.4 Moisture Trap Check

If the analyzer uses the double-bowl moisture trap previously described, use the following procedure to adjust vent flow at least once a week, or more frequently if water removal is inefficient.

1. Adjust the expansion valve to full open.
2. Adjust the back-pressure regulator on the second trap for zero vent flow.
3. Adjust the air pressure regulator on the front panel of the analyzer to about 32 psig (220 kPa). If the sample pump cannot produce 32 psig here, see section 4.7.2.
4. Adjust the back pressure regulator on the second Balston trap to obtain 30 psig (207 kPa) on the front panel gauge.
5. Adjust the expansion valve to obtain 26 psig (179 kPa) on the front panel gauge.
6. Readjust the front panel pressure to the correct operating pressure, 20-22 psig (139-152 kPa).

4.5.5 Cutter Temperature

The cutter temperature should be checked and adjusted during start-up and approximately every 6 months of operation thereafter. It should also be checked and adjusted if: (1) the cutter is replaced, (2) the cutter temperature changes, (3) the analyzer shows abnormal span drift, or (4) the CH_4 channel responds to non-methane compounds. (See section 4.7.1.8 for details.)

TABLE 10. FORM FOR RECORDING ROUTINE OPERATIONAL DATA FROM THE MSA 11-2 NMOC ANALYZER

Day	Zero Response				Span Response				Span Gas / Conc.	% Diff.		Zero Pot Setting				Span Pot Setting				Pressure Gauges					Temperature °F			Recorder Zero		
	Unadjusted		Adjusted		Unadjusted		Adjusted					Unadjusted		Adjusted		Unadjusted		Adjusted											
	CH_4	NMOC	CH_4	NMOC	CH_4	NMOC	CH_4	NMOC		CH_4	NMOC	CH_4	NMOC	CH_4	NMOC	CH_4	NMOC	CH_4	NMOC	H_2 #1	H_2 #2	Air	Oven #1	Oven #2	Oven	Overflow	Cutter	CH_4	NMOC	

4.6 CALIBRATION

This section details specific procedures for multipoint calibrations and zero and span checks of the MSA 11-2. The analyzer's instruction manual may contain deviations from these procedures, but the step-by-step procedures that follow are currently recommended by the EPA. These procedures cover the CH_4/NMOC mode of operation only (section 4.5.1)!

4.6.1 Multipoint Calibration

1. If this is an initial calibration, or if the cutter temperature is due for checking (section 4.5.5), it should be checked and adjusted prior to the calibration according to the procedure given in section 4.7.1.8.

2. To conserve calibration gas during calibration, shut off the vent flow from the moisture drop-out trap located on the back of the analyzer. Quickly check the back-pressure regulator gauges located inside the oven before and after vent flow is shut off. If the pressure reading varies before and after shutting off the moisture trap vent, trouble-shoot the back-pressure regulators located in the oven.

3. Place the range selector switch in the range most frequently used during ambient monitoring.

4. Disconnect the analyzer's sample line from the ambient manifold and reconnect it to the calibration system's manifold. Cap the port on the ambient manifold and any open ports on the calibration system's sample manifold.

5. Supply an atmosphere of the zero standard to the manifold at a flow rate that is 20 to 50% greater than the analyzer's sample flow demand. DO NOT PRESSURIZE THE ANALYZER'S SAMPLE INLET. The test atmosphere must contain an ambient level of oxygen and must not contain more than 0.1 ppmC TOC. See section 3.2 for details.

6. Adjust the analyzer's zero controls for both channels to the desired baseline responses. A 5% of full scale positive offset on the recording device is recommended to observe any negative drift. Use either the analyzer's zero pots or the recorder's controls to obtain the offset. Ensure that the responses from both channels are equal before recording the responses on forms similar to Tables 5 and 10.

7. Supply an atmosphere of methane standard to the calibration manifold at a flow rate that is 20 to 50% greater than the analyzer's sample flow demand. The methane concentration should be between 70 and 90% full scale.

8. Adjust span pot #2 (which controls CH_4 response from FID #2) to provide the analyzer response calculated as follows:

$$\text{Response} = \left(\frac{\text{Sample concentration}}{\text{URL}} \times \text{url}\right) + \text{Zero offset} \qquad (5)$$

where

Response = Response of the recording device measuring the analyzer output in recording device units.

Sample concentration = Concentration of the calibration standard delivered to the analyzer in ppmC.

URL = The upper range limit of the analyzer in ppmC.

url = The upper range limit of the recording device in recording device units.

Zero offset = The amount the recording device response is set above the zero baseline while the analyzer is measuring the zero calibration standard (in recording device units).

NOTE: The response, url, and zero offset must be in identical units. For example, if a strip chart recorder is the recording device, units will be % Chart and the url may equal 100% chart. If a digital voltmeter (DVM) is the recording device, units may be millivolts or volts and the url may be, for example, 1000 mV. If a data acquisition system (DAS) is the recording device, units may be ppmC and the url will equal 10 ppmC. If the front panel meter on the analyzer is the recording device, units will be ppmC and the url may be either 10 or 20 ppmC.

For example,

methane span concentration = 8.0 ppmC,

analyzer range being monitored = 10 ppmC

recorder range being used = 100% chart

recorder offset = 5% chart

$$\text{Response} = \left(\frac{8.0 \text{ ppmC}}{10 \text{ ppmC}} \times 100\%\right) + 5\% = 85\% \text{ chart} \qquad (6)$$

Therefore, the analyzer's span potentiometer should be adjusted until the analyzer output is equal to 85% chart on the recorder while sampling the 8.0 ppmC methane standard.

9. If step 8 results in a span pot setting greater than 300, decrease pressure to H_2 gauge #2 until the CH_4 response has increased to a point where the span pot can be reduced to about 250. If the span pot setting is less than 200, increase pressure to H_2 gauge #2 until the CH_4 response has decreased to a point where the span pot can be increased to about 250. DO NOT EXCEED 9.0 psig H_2.

> NOTE: IF THE FID RESPONSE INCREASES WHEN INCREASING HYDROGEN PRESSURE, THE BURNER IS OPERATING ON THE WRONG SIDE OF ITS PEAK RESPONSE CURVE. CONTINUE INCREASING HYDROGEN PRESSURE UNTIL RESPONSE STARTS TO DECREASE AND THE CORRECT SPAN POT SETTING IS OBTAINED. (SEE SECTION 4.7.5 IF THE PROPER RESPONSE IS UNOBTAINABLE OR IF DIFFICULTIES DEVELOP.)

10. Set span pot #1 NMOC to the same dial setting (not response) as span pot #2.

11. Repeat steps 5, 6, 7, 8, 9, and 10 if span pot adjustments were necessary or if hydrogen pressure gauge #2 was adjusted.

12. Continue sampling the methane standard. For the FIDs to be balanced, the NMOC response must be within ±1.0% of the zero response obtained in step 6. If the FIDs are balanced, go to step 14.

13. Balance detectors: If the FIDs are not balanced:

    (a) Check that both span pots are dialed to the same setting.

    (b) Locate the range change board (inside the electrometer assembly located in the oven) and rotate the balance controls of channels 1 and 2 (accessible through holes in the electrometer cover) to their maximum clockwise position. Make adjustments quickly to minimize heat loss!

> NOTE: ONLY THE 1980 11-2 MODELS HAVE ELECTROMETER BALANCE CONTROLS. USERS OF THE OLDER MODEL MUST UPDATE THEIR ANALYZER TO INCLUDE THIS MODIFICATION.

(c) Record both hydrogen pressure gauge readings. Adjust hydrogen pressure gauge #1 until the NMOC response to the methane standard equals the earlier NMOC response to the zero standard (step 6).

Do not adjust the hydrogen pressure outside the 34-62 kPa (5 to 9 psig) range. Increase hydrogen pressure to decrease NMOC response, or vice versa. See the note in step 9.

(d) If balance is achieved, repeat steps 5 through 13.

(e) If balance is not achieved by step c, adjust the NMOC hydrogen pressure (gauge #1) or both hydrogen pressures, if necessary, to get as close to balance (NMOC response within ± 1% of NMOC zero response) as possible. Do not exceed the 34-62 kPa (5-9 psig) hydrogen pressure range. Then, using the balance controls on the range change board located inside the electrometer (accessible through holes in the electrometer cover), rotate the channel #2 balance control counter-clockwise to increase the NMOC response, or rotate the channel #1 balance control counter-clock wise to decrease the NMOC response. Repeat steps 5 through 12. If balance cannot be achieved, see section 5.7.5.

14. After the FIDs are balanced, record responses on Tables 5 and 10. Determine the CH_4 channel's response to two or more additional concentrations of the methane standard that are spaced approximately equally over the analyzer range. (The NMOC channel's response should remain equal to the earlier response to zero standard.) Record the CH_4 and NMOC channel's responses (from the recording device) on Table 5. Using a calculator, perform a least squares linear regression of the CH_4 channel responses (to methane and zero standards) and the corresponding calibration concentrations. The calibration concentrations should be in units of ppmC and should be entered into the calculator as the independent variable X. The CH_4 channel's response should be in units of the recording device and should be entered as the dependent variable Y. A correlation coefficient (r) of 0.9996 or better verifies that the CH_4 response is linear. (If the response is not linear, plot the data and determine if an error has been made in data entry or in determination of calibration concentration.) Obtain the slope and intercept of the regression and record the equation in the following form:

$$CH_4 \text{ Response} = CH_4 \text{ Slope} \times \text{Methane concentration} + CH_4 \text{ Intercept} \quad (7)$$

where

CH_4 Response = Analyzer's CH_4 channel reading in recording device units (see note following step 8).

CH_4 Slope = Regression slope in recording device units per ppmC.

Methane concentration = Calibrated methane concentration in ppmC.

CH_4 Intercept = Regression intercept in recording device units.

Post the CH_4 channel's multipoint calibration curve equation on the analyzer's recording device and also on Tables 5 and 10.

15. Supply an atmosphere of propane standard to the calibration manifold at a flow rate that is 20 to 50% greater than the analyzer's sample flow demand. The propane concentration should be between 70 and 90% of full scale.

16. Adjust span pot #1 (which controls NMOC response from FID #1) to provide the desired analyzer response. Equation 5 in step 8 can be used here.

17. If an adjustment is made in step 16, recheck the NMOC channel's response to the zero standard and adjust zero pot #1 if necessary. Record the stable zero responses from the NMOC and CH_4 channels. Sample the propane standard, and again record the stable responses to propane. (CH_4 response should be equal to the earlier response to zero air.)

18. Determine the NMOC channel's response to two or more additional concentrations of the propane standard that are spaced approximately equally over the analyzer range. (The CH_4 channel's response should remain equal to the earlier response to zero standard.) Record the NMOC and CH_4 channel's responses (from the recording device) on Table 5. Using a calculator, perform a least squares linear regression of the NMOC channel's response (to propane and zero standards) and the corresponding propane calibration concentrations. The calibration concentrations should be in units of ppmC and should be entered into the calculator as the independent variable X. The NMOC channel's response should be in units of the recording device and entered as the dependent variable Y. A correlation coefficient (r) of 0.9996 or better verifies that the NMOC response is linear. (If the response is not linear, plot the data and determine if an error has been made in data entry or in determination of calibration concentration.) Obtain the slope and intercept of the regression and record the equation in the following form:

NMOC Response = NMOC Slope x NMOC Concentration + NMOC Intercept (8)

where

NMOC Response = Analyzer's NMOC channel reading in recording device units (see note following step 8).

NMOC Slope = Regression slope in recording device units per ppmC.

NMOC Concentration = Calibrated NMOC concentration in ppmC.

NMOC Intercept = Regression intercept in recording device units.

Post the NMOC channel's multipoint calibration curve equation on the analyzer's recording device and on Tables 5 and 10. Record all zero and span pot readings in Table 10.

19. Disconnect the analyzer's sample line from the calibration system's manifold and reconnect it to the ambient manifold.

20. Follow the procedure in section 4.5.4 to reset the moisture trap vent flow rate.

21. Record readings from the first seven analyzer parameters listed in Table 10. These readings will now be the reference readings until another multipoint calibration is performed. Be certain that the station logbook, strip charts, etc., are properly annotated, dated, and initialed.

22. If level 2 zero and span checks are to be used, carry out such a check now to establish reference zero and span readings for subsequent comparison. (See section 2.0.9.1.3 of reference 10 for definitions and additional information on level 1 and 2 zero and span checks.)

4.6.2 Level 1 Zero/Span Check

The following level 1 zero/span check (2-point calibration) is similar to a multipoint calibration except only the zero air standard and one upscale standard are used. These responses are then used to calculate the new calibration curve which is used to correct subsequent monitoring data until another level 1 zero/span check or multipoint calibration is performed. As part of an overall quality assurance program, the operator may want to record unadjusted responses to standards before making any changes to operational parameters or zero and span potentiometers.

1. Disconnect the analyzer's sample line from the ambient manifold and reconnect it to the calibration system's output sampling manifold. Cap the sample port on the ambient manifold and any open ports on the calibration system's sample manifold.

2. To conserve calibration gas during calibration, shut off the vent flow from the moisture trap located on the back of the analyzer. Quickly check the back-pressure regulator gauges located inside the oven immediately before and after the moisture trap vent is shut off. If the pressure reading varies before and after shutting off the moisture trap vent, troubleshoot the back-pressure regulators located in the oven.

3. Supply an atmosphere of the zero standard to the calibration manifold at a flow rate of 20 to 50% greater than the analyzer's sample flow demand. DO NOT PRESSURIZE THE ANALYZER'S SAMPLE INLET.

4. After obtaining a stable zero reading, determine if zero drift is greater than about ± 3.0% (see section 3.8 for zero drift calculation).

   If necessary, adjust the analyzer's zero pots to obtain the correct responses. Record the zero responses on forms similar to Tables 6 and 10.

5. Supply an atmosphere of methane standard to the calibration manifold at a rate 20 to 50% greater than the analyzer's sample flow demand. The methane concentration should be between 70 and 90% full scale.

6. After obtaining a stable CH_4 reading, use the span drift equation from section 3.8 (Equation 4) to calculate the amount of span drift on the CH_4 channel. If the drift is greater than about ± 7.0%, perform steps 8 through 21 in the multipoint calibration procedure in section 4.6.1. (Linearity assessment is not necessary in steps 14 and 18.)

7. If span drift is within specifications, check to see that the NMOC channel's response is within ± 1.0% of the NMOC channel's earlier response when sampling the zero standard. If so, the FIDs are balanced. If the FIDs are not balanced, perform steps 8 through 21 in the multipoint calibration procedure, section 4.6.1. (Linearity assessment is not necessary in steps 14 and 18.)

8. If the span drift is less than about ± 7.0% and the FIDs are balanced, record the response and determine the slope and intercept of the CH_4 channel's level 1 calibration curve. Post the level 1 calibration curve equation on the analyzer's recording device and on Tables 6 and 10.

9. Supply an atmosphere of propane standard to the calibration manifold at a rate 20 to 50% greater than the analyzer's sample flow demand. The propane concentration should be between 70 and 90% of full scale.

10. After obtaining a stable span reading, use the span drift equation from section 3.8 (Equation 4) to calculate the amount of span drift on the

NMOC channel. If the drift is greater than about + 7.0%, adjust span pot #1 to provide the proper analyzer response. (Use Equation 5 in step 8, section 4.6.1, to calculate response.)

11. Record the responses and determine the slope and intercept of the NMOC channel's level 1 calibration curve. Post the NMOC channel's level 1 calibration curve equation on the analyzer's recording device and in Tables 6 and 10. Record all zero and span pot readings on Table 10.

12. Reconnect the sample line to the ambient manifold.

13. Reopen the moisture trap vent and adjust vent flow according to the procedure given in section 4.5.4.

14. If level 2 zero and span checks are to be used, carry out such a check now to establish reference zero and span readings for subsequent comparison.

4.7 TROUBLESHOOTING

The manufacturer's instruction manual covers this subject under the same heading. Additional comments follow.

4.7.1 Preliminary Investigations

Operational problems such as slow response to standards (response time greater than 10 seconds), inability to balance FID responses, long stabilization periods (greater than 5 minutes), frequent flame-outs, or low sensitivity indicate the potential need for in-depth troubleshooting. Prior to undertaking in-depth troubleshooting, a preliminary investigation is recommended to rule out variations in operational parameters.

1. Check that all pressure gauges on the analyzer are set to the specifications stated on the Manufacturer's Final Data Sheet (or to the specifications stated in Table 9 if a manufacturer's data sheet is not available). If the analyzer has been operating properly for several months, ensure that the pressure gauges are set to the readings recorded during the most recent multipoint calibration when the FIDs were balanced.

2. Inspect the hydrogen source and hydrogen filters (located outside the analyzer) for proper operation. If neither hydrogen pressure gauge on the analyzer can be adjusted to its proper setting, see section 4.7.4.

3. Inspect the sample filter and replace it if dirty. Replace the sample line leading to the analyzer if particulate buildup is noticeable.

4. Perform the moisture trap setup procedure outlined in section 4.5.4. If the sample pump cannot produce 32 psig head pressure during the procedure, see section 4.7.2.

5. Determine if the sample vent flow rates through the back-pressure regulators (located in the oven) are within specifications.

   (a) Open the door and connect tubing to a back-pressure regulator vent.

   (b) Run the tubing outside the oven and tape the door closed. Do not crimp the tubing.

   (c) Connect a flow meter to the tubing and measure the flow rate. The rate should be approximately 500 cm^3/min.

   (d) If the flow rate from either vent differs by more than 5% from the flow rate measured during the most recent period of normal operation, see section 4.7.2.

6. Measure the sample flow rates into the FIDs.

   (a) Disconnect a sample line from the base of the FID.

   (b) Connect an adapter to the nut of the sample line.

   (c) Connect tubing to the adapter, run the tubing out of the oven, and tape the oven door closed. Do not crimp the tubing.

   (d) Connect a flow meter to the tubing and measure the flow rate. The rate should be between 10 and 15 cm^3/min.

   (e) If either sample flow rate differs by more than 5% from the flow rate measured during the most recent period of normal operation, see section 4.7.6.

7. Measure the burner air flow rates into the FIDs.

   (a) Disconnect a burner air line from the side of the FID.

   (b) Connect an adapter to the nut on the burner air line.

   (c) Connect tubing to the adapter, run the tubing out of the oven, and tape the oven door closed. Do not crimp the tubing.

   (d) Connect a flow meter to the tubing.

   (e) Measure the flow rate. The rate should be approximately 200 ± 50 cm^3/min.

(f) If either burner air flow rate differs by more than 5% from the flow rate measured during the most recent period of normal operation, see section 4.7.7.

8. Perform the cutter temperature adjustment procedure.

(a) Locate the "cutter temperature card" in the top of the analyzer. (See instruction manual for location and detailed photograph of the card.)

(b) Sample a methane standard until a stable methane response is obtained.

(c) Slowly increase cutter temperature (wait 30 minutes after each adjustment) until a decrease in methane response is noticed.

(d) Allow the response to stablize (1 hour) and record the temperature as T_1.

(e) Slowly reduce the cutter temperature and observe the increasing methane response.

(f) When methane response cannot be increased by a further cutter temperature decrease, allow the response and temperature to stabilize and record the temperature as T_2.

(g) The difference between T_2 and T_1 should be at least 7° C (10° F). If not, decrease T_2 until the difference is obtained. No change in methane response should occur.

4.7.2 Sample Pump System Investigation

The sample pump supplies the sample, burner air, moisture trap vent, and sample vent to specific areas in the analyzer. Deterioration of the pump, blockages in flow systems, or leaks in flow systems can alter the flow rate of one or more of these critical flows. If preliminary investigations identify a significant change in the sample vent flow rate (flow rate differs by more than 5% from the flow rate measured during the most recent period of normal operation), or the proper AIR pressure reading cannot be obtained or the sample pump cannot produce at least 32 psig during the moisture trap setup, carry out the following investigation.

1. Inspect the sample filter and intake to the pump for obstructions.

(a) Clean or replace as necessary.

2. Inspect the tubing between the pump outlet and AIR pressure gauge for an obvious leak (hissing will be detected).

(a) Repair or replace the leaky element.

3. If adjustments were made in steps 1 or 2, remeasure the sample vent flow rate (4.7.1.5). If flow rates are not within 400 to 600 cm^3/min:

   (a) Adjust the flow control valve located inside the analyzer (see flow diagram in the instruction manual).

   (b) If the flows cannot be properly adjusted, ensure that the sample pump is functional before replacing the back-pressure regulator.

4. Perform the moisture trap set up procedure (4.5.4).

   (a) If the pump pressure cannot produce 32 psig, clean or replace the pump diaphragm.

4.7.3 Moisture Trap Investigation

If the second moisture trap begins accumulating water, immediately investigate the system.

1. Ensure that the first moisture trap is neither flooded nor installed in reverse. (Observe the arrows located on the top of the trap for flow direction.)

2. Perform the setup procedure outlined in section 4.5.4.

3. Perform troubleshooting steps in section 4.7.2.

4.7.4 Hydrogen System Investigation

If the hydrogen pressure gauge readings begin to drift, investigate the system.

1. Ensure that the hydrogen source is not depleted and that no leaks or obstructions exist in the tubing delivering the gas to the analyzer.

2. Measure the hydrogen flow rate to the FID.

   (a) Disconnect a hydrogen line from the side of the distribution manifold.

   (b) Connect an adapter to the fitting located on the side of the distribution manifold.

   (c) Connect tubing to the adapter, run the tubing out of the oven, and tape the oven door closed. Do not crimp the tubing.

   (d) Connect a flow meter to the tubing.

   (e) Depress the ignitor button on the front panel to allow hydrogen gas to flow through the flow meter.

(f) Measure the flow rate. The rate should be approximately 15 to 20 cm^3/min.

(g) If the flow rate differs by more than 5% from the flow rate measured during the most recent period of normal operation, see step 3 below.

3. Inspect the hydrogen restrictors in the fittings connected to the distribution manifold for debris and clean or replace as necessary. (Clean or replace both fittings if one needs cleaning or replacing.)

(a) Remove the hydrogen line fitting from the exit side of the distribution block.

(b) Soak the fittings in a solvent (methyl alcohol) for several hours (ultrasonic bath can hasten the cleaning).

(c) Connect a clean air pressure line to the outlet of the fitting and force air through the fitting (in reverse) while the fitting is submerged in solvent.

(d) After unrestricted flow is obtained through the fitting, remove the fitting from the solvent and continue to pass air through it until all solvent is evaporated.

(e) Install the cleaned restrictor and measure the hydrogen flow.

4. Determine if any other part of the hydrogen flow system contains obstructions. If so, replace or attempt to clean by reverse flushing with methyl alcohol.

5. Leak test the hydrogen flow system and determine if a leak is present. (Use the procedure detailed in section 2.4.2.)

6. Check the hydrogen gauge for possible malfunctions.

4.7.5 FID Response Investigation

If the FID response increases with increasing hydrogen pressure, or the FIDs cannot be balanced, or the factory-specified pressure or flow settings do not produce satisfactory analyzer operation, and no flow abnormalities exist, new settings must be established. The complex interrelationship between hydrogen pressure, hydrogen flow, and FID response for the two burners makes this difficult to do by trial and error. A better approach is to determine the complete pressure-flow and flow-response relationships for each FID over a wide range, and then use these relationships to pick a viable operating point.

1. Measure hydrogen flow rates into the FIDs at several different hydrogen pressure settings. Cover the 5 to 9 psig range of the gauges and plot flow rates against pressure gauge readings.

2. Measure both sample flow rates into the FIDs.

3. Reset the moisture trap vent flow to ensure that it is properly adjusted (see 4.5.4).

4. Place the jumper on the electrometer card in the N (non-subtracting) position to permit recording of the TOC and CH_4 responses. Adjust the two electrometer balance controls to their maximum clockwise position and the two span controls to their maximum position. Allow the analyzer to re-establish thermal equilibrium.

5. Disconnect the analyzer's sample line from the ambient manifold and reconnect it to the calibration system's manifold.

6. Supply an atmosphere of methane standard to the calibration manifold at a rate 20 to 50% greater than the analyzer's sample flow demand.

   The methane concentration should be between 70 and 90% full scale.

7. Reduce hydrogen pressure on gauges #1 and #2 until each gauge reads 5.0 psig (35 kPa). (If a flame-out occurs, increase H_2 pressure to the point where the flame can be sustained.) Record the hydrogen gauge readings, along with the corresponding response (H_2 #1 controls TOC response and H_2 #2 controls CH_4 response).

8. Increase both hydrogen pressure gauge readings in intervals of 0.5 to 1.0 psi. Record stable responses from both channels to each hydrogen pressure reading. Continue increasing hydrogen pressure up to 9.0 psig (62 kPa). Operating the burners at high hydrogen flow rates for extended periods may be detrimental to the burner components; therefore, return hydrogen pressure to 7.0 psig after obtaining the last response.

9. Repeat step 8 while sampling the zero air standard.

10. Using the hydrogen pressure-flow relationship from step 1, calculate the hydrogen to sample flow rate ratios for each hydrogen setting. Plot the hydrogen to sample flow rate ratios on the abscissa, and the corresponding analyzer responses to methane and zero on the ordinate for each FID. NOTE: Analyzer response to methane should be the net response. Net response is the actual methane response less the zero response at each hydrogen pressure setting. See Figures 5 and 6.

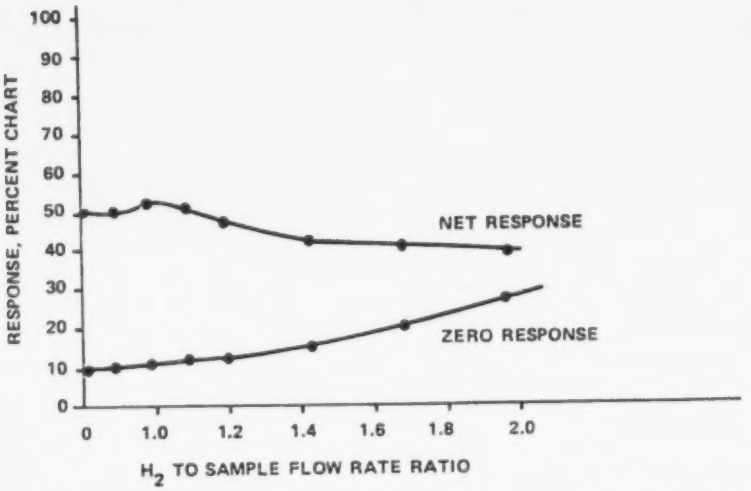

Figure 5. CH_4 channel's response curves—effects of variations in H_2 flow rate. Sample flow rate @ 10.2 cm^3/min, net response = response to constant methane concentration less response to zero air.

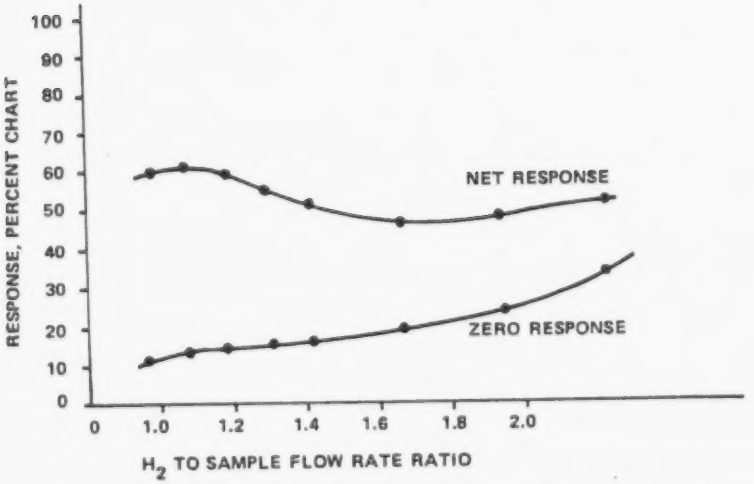

Figure 6. TOC channel's response curves—effects of variations in H_2 flow rate. Sample flow rate @ 10.2 cm^3/min, net response = response to constant methane concentration less response to zero air.

11. If either response curve contains a peak, adjust the hydrogen pressures to selected values which produce approximately equal CH_4 and TOC responses. Preferably, the resulting hydrogen setting should be near or somewhat to the right of the peak response hydrogen setting.

12. If the response curves from step 10 do not contain a peak, or if the peak is contained on a broad plateau, adjust the hydrogen pressures to selected values which produce approximately equal CH_4 and TOC responses, preferably at hydrogen to sample ratios of about 1.0 to 1.4.

13. Reconnect the sample line to the ambient manifold and place the jumper on the electrometer card in the S (subtracting) position to permit recording of NMOC and CH_4 responses.

14. Recheck analyzer operation to see if proper balance and calibration can now be achieved. If not, pick new operating points from the response curves, adjust parameters, and recheck analyzer operation.

4.7.6 Sample Flow Rate Investigation

If either sample flow rate to the FID (4.7.1.6) differs by more than 5% from the flow rate measured during the most recent period of normal operation and the sample pump system has been eliminated as the problem (section 4.7.2), carry out the following investigation.

1. Ensure that both sample capillaries produce the same flow when connected to the same outlet of the distribution manifold. If flows are not within $\pm$ 0.2 cm^3/min of each other, clean both in an ultrasonic bath of methyl alcohol, and then recheck flow rates. If differences still exist, order new, matched capillaries from the manufacturer.

2. Determine if any other part of the sample flow system contains obstructions. (Measure flow rates from both sample ports of the distribution manifold. They should be equal. If not, measure the flow rate entering and exiting the cutter. If these flow rates are not equal, the cutter is clogged. Replace the cutter and check flow rates.)

3. Leak test the sample flow system. (Use the procedure detailed in section 2.4.2.)

4.7.7 Burner Air Flow Rate Investigation

If either burner air flow rate to the FID (4.7.1.7) differs by more than 5% from the flow rate measured during the most recent period of normal operation, and if the sample pump system has been eliminated as the problem (4.7.2), carry out the following investigation.

1. Inspect the burner air restrictors in the distribution manifold for debris and clean or replace as necessary. (If one needs cleaning or replacing, clean or replace both restrictors.)

   (a) Remove the burner air line from the exit side of the distribution block.

   (b) Soak the fittings in a solvent (methyl alcohol) for several hours (an ultrasonic bath can hasten the cleaning).

   (c) Connect a clean air pressure line to the outlet of the fitting and force air through the fitting (in reverse) while the fitting is submerged in solvent.

   (d) After free flow is obtained through the restrictor, remove the fitting from the solvent and continue to pass air through it until all solvent has evaporated.

   (e) Install the cleaned restrictor and measure the burner air flow as before.

2. Determine if any other part of the burner air flow system contains obstructions. If so, replace or attempt to clean by reverse flushing with methyl alcohol. (If any obstruction is located in the oxidizer, replace or repack the unit.)

3. Leak test the burner air system and determine if a leak is present. (Use the procedure detailed in section 2.4.2.)

SECTION 5

AUGMENTED PROCEDURES FOR THE BENDIX 8201 AND 8202 REACTIVE HYDROCARBON ANALYZER

NOTE: READING SECTIONS, 1, 2, AND 3 BEFORE SECTION 5 IS STRONGLY RECOMMENDED. INFORMATION WHICH IS CRITICAL TO THE UNDERSTANDING AND SUBSEQUENT ACCURATE OPERATION OF THIS ANALYZER IS DETAILED IN THOSE SECTIONS AND WILL NOT BE REPEATED HERE.

The manufacturer has prepared a relatively detailed instruction manual which can guide users during installation and operation of the model 8201 and 8202 analyzers. The thoroughness of the manual will therefore allow this section to be brief. As stated in the introduction, the purpose of this TAD is to supplement the analyzer's instruction manual by augmenting critical installation and operation procedures.

5.1 PRINCIPLES OF OPERATION

The analyzer's instruction manual contains a discussion on this subject in the "Introduction". In the discussion the term "mechanical separating device" is used in place of chromatographic column; and the "detector" cell is a hydrogen flame ionization detector (FID). Both analyzer models have essentially the same design, so a brief summary of their operation follows.

The analyzers contain one FID and one sample loop. At the start of the 200 second cycle, sample is directed from the sample loop into the mechanical separating device. The methane component of the sample emerges first and is injected into the FID for measurement. As the separating device is back-flushed, another sample from the sample loop is directed straight to the FID for measurement of TOC. Internal subtraction of the CH_4 and TOC measurements results in the NMOC reading.

5.2 SYSTEM DESCRIPTION

A detailed description of the analyzer is given in the analyzer's instruction manual. This TAD will therefore not address location of components, but will emphasize the uses and precautions of those which are critical.

5.2.1 Flame Ionization Detector

The analyzer contains one FID. The separate responses of the CH_4 and TOC channels must be balanced to a methane-in-air standard.

5.2.2 Hydrogen Pressure Gauge

The flow of hydrogen fuel to the FID is controlled by a pressure regulator, gauge, and restrictor. Increasing the pressure reading on the hydrogen gauge will increase the flow of hydrogen to the burner and affect the sensitivity of the FID.

5.2.3 Flameout Indicator

If a condition exists which causes the hydrogen flame in the FID to extinguish, the analyzer will either automatically attempt reignition or will shut off flow of hydrogen to the FID. The action is determined by the position of toggle switch S7 located on the front panel. In the event of a flame-out, the flame-out indicator will illuminate. If the status of the flame is in doubt, observe analyzer response first to zero air and then to a sample known to contain hydrocarbon. If the TOC channel's responses are the same to both samples, the flame is out.

5.2.4 Sample/Back-Flush Valves

The O-rings of these two valves are susceptible to wear and thus leakage. Replace O-rings in both valves every 6 months, or sooner if leaks develop. The 8202 manual contains details on specific leak-check procedures. A procedure for leak-checking these valves, and the sample flow system, is detailed in section 5.7.3 of this TAD.

5.2.5 Columns

To prevent column contamination, the columns should be capped whenever they are removed from the analyzer or whenever the analyzer is powered-down for an extended period of time.

5.3 MODIFICATIONS

The model 8201 analyzer has been slightly modified to produce the model 8202. The principle of operation and detection is unchanged. Differences between the two models follow.

5.3.1 Relocation of Timer

The MANUAL CYCLE POSITION TIMER and the CH_4, THC and ZERO FUNCTION LIGHTS have been moved from inside the 8201 analyzer to the front panel of the 8202.

5.3.2 Instruction Manual

The analyzer instruction manual has been rewritten.

5.3.3 Calibration Procedure

The calibration procedure for the 8202 calls for a zero air standard and three methane/ethane in air span standards. (See section 5.6 for the EPA recommended calibration procedure.) The sequence of events during calibration, zero/span checks, and electronic timing has been changed.

5.3.4 "California" Modification

At monitoring sites where significant concentrations of "heavy" hydrocarbons exist, a problem may arise with the Bendix analyzer which causes the TOC reading to be too low. The cause of the low TOC reading is that during the TOC measurement, the methane and heavy hydrocarbons may separate due to the chromatographic action of the surfaces of the lines and components with which the sample comes in contact. This causes the normal TOC peak on the FID to separate into 2 distinct peaks, one for methane and light compounds and the other for the heavier compounds. The height of these separate peaks is less than the height of a single combined peak. Since the analyzer detects only peak height and not peak area, the resulting TOC reading is reduced by the separation.

This TOC peak separation may be worse with some analyzers than with others. A test for the effect is to run a chromatogram (see section 5.7.2) using a mixture of methane and a heavier compound such as m-xylene. If separation is occurring, it will show up as a separation of the TOC peak into separate peaks in the chromatogram.

A modification to the analyzer to reduce the effect of this TOC separation has been developed by Bendix for certain California monitoring agencies. The modification may become standard for new model 8202 analyzers, and Bendix will likely offer a kit to modify existing instruments. The modification consists of a new chromatographic column, a new capillary, and some plumbing changes. It also includes a change in the operation of the analyzer such that the TOC reading is obtained first and the CH_4 reading last. This means that the valve and gate timing must be changed. For analyzers incorporating this modification, appropriate changes must be made to the instructions in section 5.7.2. Consult the Bendix Corporation for further details on this modification.

5.4 INSTALLATION

The analyzer's instruction manual contains a discussion on the subject under the same heading. Additional comments follow.

5.4.1 General Comments

1. Before supplying power to the analyzer, ensure that all electronic cards are properly seated by attempting to push the cards snugly into the connectors.

2. Minimize the distance between the analyzer and the sample manifold. Use clean, 3 mm (1/8 in) diameter inert tubing to make the sample line. The sample line length should not exceed 3 m (10 ft).

3. Leak-checks should be made on the hydrogen flow system of old and new analyzers. See the instruction manual for details or use the procedure in section 2.4.2 of the TAD.

> CAUTION: ONLY EXPERIENCED, QUALIFIED OPERATORS SHOULD PERFORM THE LEAK CHECK. AVOID FINGER CONTACT WITH THE FITTING THREADS DUE TO POSSIBLE TRANSFER OF OILS THAT WILL TEMPORARILY INCREASE THE BASELINE RESPONSE.

4. Hydrogen gas, burner air, and carrier air should not contain TOC contaminant concentrations that can not be "bucked-out" by the auto zero. (Perform a level 1 zero and span check after replacing any of these support gases.)

5. If zero air is used to dilute span gases, it must not contain more than 0.1 ppmC TOC concentration.

6. Connect a recorder to the NMOC output located in the rear panel of the analyzer. If desired, recorders can also be connected to the analyzer's TOC and CH_4 outputs. A temporary, multiple speed recorder capable of operating at ~16 in per hour is necessary for recording chromatograms from the analyzer's front panel jack.

7. Do not connect calibration gas to the CALIBRATE port.

8. The needle valves located inside the analyzer (NDLV 1) and oven (NDLV 2 and 3) can be accessed through small holes drilled through the analyzer cover and oven. Knobs on the valves can be removed, leaving the stem to be adjusted by a long screwdriver. This modification enables flow rate adjustments without removing the analyzer cover and oven top, which eliminates heat loss and subsequent flow rate instabilitly during adjustments.

5.4.2 Sample Pump Installation

The instruction manual specifies installing the sample pump outlet to the SAMPLE port on the rear of the analyzer. In this configuration, the sample passes through the pump before analysis by the analyzer. However, a very simple modification allows the pump to draw the sample through the sample loop in the analyzer such that the sample does not pass through the pump first. The modification consists of connecting the inlet of the sample pump to the CALIBRATE port of the analyzer and turning the front panel selector switch to the calibrate position. This switch must be left in the CALIBRATE position during normal operation. Sample air will thus be drawn into the SAMPLE VENT port and out the CALIBRATE port to the pump. In this mode, the flow is adjusted with the sample needle valve (006718-2), as the back pressure regulator on the rear panel will have no effect.

5.5 OPERATION

5.5.1 Start-Up

The analyzer's instruction manual covers this discussion under "Operation". Additional comments follow.

1. After supplying power and support gases to the analyzer, allow the analyzer to operate for several hours to enable temperatures and flow rates to stabilize; then measure flow rates. Use good laboratory procedures in measuring flow rates. (See section 3.6 in this TAD for guidance during flow measurements.)

2. The model 8201 instruction manual specifies normal settings or ranges for most of the operational parameters. If a Manufacturer's Final Data Sheet (Bendix's Factory Test Data Sheet) is not available with the analyzer, set the parameters as specified in the instruction manual, or to previously used values.

5.5.2 Periodic Calibrations and Zero/Span Checks

An initial multipoint calibration is recommended to verify linearity in the calibration curve. Periodic level 1 zero and span checks are thereafter necessary to update the calibration curve. The frequency of level 1 zero and span checks and subsequent multipoint calibrations should be based on the analyzer's performance. Performance can be monitored through the use of a control chart which documents responses to standards and ultimately enables calculation of variation in response to standards (drift). (See section 2.0.9 of reference 10 for details on calibrations and level 1 and level 2 zero and span checks. See section H of reference 14 for details on control charts. See section 5.6 of this TAD for calibration procedures.)

5.5.3 Operational Checks

The analyzer's operational parameters should be checked at least once a week, or more frequently if necessary. Parameters that should be routinely checked and recorded on Table 11 are pressure gauge readings, analyzer responses, and other routine checks that may be necessary. (Routine monitoring may not require that unadjusted responses to standards be recorded; however, special cases may warrent such data.) If any of these parameters shows substantial change from the last check, recheck the analyzer calibration with a level 1 zero and span check and make the necessary adjustments.

5.5.4 Routine Chromatograms

A chromatogram (Bendix uses the term "spectrum") should be evaluated during start-up and on a weekly basis thereafter to determine if analyzer parameters have shifted outside the limits of proper operation. Critical parameters, such as gate timing, FID sensitivity, and flow rates can be investigated through careful evaluation of the chromatogram. See section 5.7.2 for procedures to obtain a chromatogram, methods to evaluate the chromatogram, and adjustments to correct improper analyzer operation.

5.6 CALIBRATION

This section details specific procedures for multipoint calibrations and zero and span checks of the Bendix 8201 and 8202. The analyzer's instruction manual may contain deviations from these procedures, but the step-by-step procedures that follow are currently recommended by the EPA.

5.6.1 Multipoint Calibration

1. Disconnect the analyzer's sample line from the ambient sample manifold and reconnect it to the calibration system's manifold. Cap the port on the ambient manifold, and on any open ports on the calibration system's manifold.

2. Place the analyzer's range selector switch in the desired concentration range. (Calibrate the analyzer on the range normally used during ambient sampling.) Ensure that the TIMER and VALVE toggle switches are in the AUTO position.

3. Supply an atmosphere of methane-in-air to the calibration manifold at a flow rate that is 20 to 50% greater than the analyzer's sample flow demand. DO NOT PRESSURIZE THE ANALYZER'S SAMPLE INLET.

4. Run a chromatogram (at least once a week) and evaluate it for proper analyzer operation (gate timing, flow rates, etc; see section 5.7.2 for

TABLE 11. FORM FOR RECORDING ROUTINE OPERATIONAL DATA FROM THE BENDIX 8201 OR 8202 NMOC ANALYZER

Day	Zero Response						Span Response						Span Gas / Conc.	% Diff.			Zero Pot Setting						Span Pot Setting						Pressure Gauges			Recorder Zero
	Unadjusted			Adjusted			Unadjusted			Adjusted							Unadjusted			Adjusted			Unadjusted			Adjusted			Air		H_2	
	TOC	CH_4	NMOC	TOC	CH_4	NMOC	TOC	CH_4	NMOC	TOC	CH_4	NMOC		TOC	CH_4	NMOC	TOC	CH_4	NMOC	TOC	CH_4	NMOC	TOC	CH_4	NMOC	TOC	CH_4	NMOC	Burner	Carrier		

MONTH

procedures). Allow the analyzer to stabilize before continuing calibration.

5. Supply an atmosphere of the zero standard to the sample manifold at a flow rate 20 to 50% greater than the analyzer's sample flow demand. DO NOT PRESSURIZE THE ANALYZER'S SAMPLE INLET. The test atmosphere must contain an ambient level of oxygen and must not contain more than 0.1 ppmC TOC. (See section 3.2 for details.)

NOTE: THE ANALYZER'S AUTO ZERO WILL CORRECT FOR MINOR CONTAMINATION IN THE HYDROGEN, BURNER AIR, AND CARRIER AIR, BUT WILL NOT CORRECT FOR ZERO GAS CONTAMINATION. DISCREPANCY BETWEEN THE AUTO-ZERO LEVEL AND THE ZERO-AIR RESPONSE MAY INDICATE CONTAMINATED ZERO AIR.

6. Adjust the TOC zero pot, CH_4 zero pot, and the NMOC zero pot to obtain the desired baseline. (A 5% full scale offset is recommended to observe negative drift.) The THC, CH_4, NMOC sequence must be followed if subsequent adjustments are necessary. Ensure that readings from all channels are equal before recording them on Tables 5 and 11.

7. Supply an atmosphere of the methane standard to the sample manifold at a flow rate 20 to 50% greater than the analyzer's sample flow demand. DO NOT PRESSURIZE THE ANALYZER'S SAMPLE INLET. Methane concentration should be between 70 and 90% full scale.

8. Adjust the front panel CH_4 and TOC span pots to provide the analyzer response calculated as follows:

$$\text{Response} = \frac{\text{Sample concentration}}{\text{URL}} \times \text{url} + \text{zero offset} \qquad (9)$$

where

Response = Response of the recording device measuring the analyzer output in recording device units.

Sample Concentration = Concentration of the calibration standard delivered to the analyzer in ppmC.

URL = The upper range limit of the analyzer in ppmC.

url = The upper range limit of the recording device in recording device units.

Zero offset = The amount the recording device response is set above the zero baseline while the analyzer is measuring the zero calibration standard (in recording device units).

NOTE: The response, url, and zero offset must be in identical units. For example, if a strip chart recorder is the recording device, units will be in percentages of chart and the url may equal 100% chart. If a digital volt meter (DVM) is the recording device, units may be in millivolts or volts and the url may be, for example, 1000 mV. If a Data Acquisition System (DAS) is the recording device, units may be in ppmC and the url will equal 10 ppmC. If the front panel meter on the analyzer is the recording device, units will be in ppmC and the url may be 10 ppmC.

Record the stable responses on Tables 5 and 11.

9. If either span pot is adjusted, recheck the zero and then the methane responses (Steps 5 through 9). Ensure that all channels' responses to the zero standard are within ± 1.0% of zero, that the CH_4 and THC responses to the methane standard are within ± 1.0% of the actual concentration, and that the NMOC response to the methane standard is within ± 1.0% of the NMOC response to the zero standard.

10. Determine the CH_4 and TOC channels' responses to two or more additional concentrations of the methane standard that are approximately equally spaced over the analyzer range. (The NMOC channel's response should remain equal to the earlier zero standard response.) Record the CH_4 and TOC channels' responses (from the recording device) on Table 11. Using a calculator, perform a least squares linear regression of the CH_4 channel responses (to methane and zero standards) and the corresponding calibration concentrations. The calibration concentrations should be in units of ppmC and should be entered into the calculator as the independant variable X. The CH_4 channel's responses should be in units of the recording device and should be entered as the dependent variable Y. A correlation coefficient (r) of 0.9996 or better verifies the CH_4 response as linear. (If the response is not linear, plot the data and determine if an error has been made in data entry or in determination of a calibration concentration.) Obtain the slope and intercept of the regression and record the equation in the following form:

$$CH_4 \text{ Response} = CH_4 \text{ Slope X Methane Concentration} + CH_4 \text{ Intercept} \quad (10)$$

where

CH_4 Response = Analyzer's CH_4 channel reading in recording device units (see note following step 8).

CH_4 Slope = Regression slope in recording device units per ppmC.

Methane Concentration = Calibrated methane concentration in ppmC.

CH_4 Intercept = Regression intercept in recording device units.

Post the CH_4 channel's calibration curve equation on the analyzer's recording device and also on Tables 5 and 11. Also, using the above equation and the TOC responses, determine the TOC calibration curve and post it accordingly.

11. Supply an atmosphere of the propane standard to the sample manifold at a flow rate 20 to 50% greater than the analyzer's sample flow demand. DO NOT PRESSURIZE THE ANALYZER'S SAMPLE INLET. Propane concentration should be between 70 and 90% full scale.

12. Adjust only the NMOC span pot to provide the analyzer response calculated from equation in 9 step 8. If the NMOC span pot is adjusted, recheck the NMOC response to the zero standard and adjust the zero pot if necessary. Recheck the NMOC response to the propane standard. Record the stable responses on Tables 5 and 11.

13. Determine the NMOC channel's response to two or more additional concentrations of the propane standard that are spaced approximately equally over the analyzer range. The CH_4 channel's response should remain equal to the earlier response to zero standard. Record the stable responses (from the recording device) on Table 5. Using a calculator, perform a least squares linear regression of the NMOC channel's response (to propane and zero standards) and the corresponding propane calibration concentrations. The calibration concentrations should be in units of ppmC and should be entered into the calculator as the independent variable X. The channel's response should be in units of the recording device and should be entered as the dependent variable Y. A correlation coefficient (r) of 0.9996 or better verifies that the response is linear. (If the response is not linear, plot the data and determine if an error has been made in data entry or in determination of calibration concentration.) Obtain the slope and intercept of the regression and record the equation in the following form:

NMOC Response = NMOC Slope X NMOC Concentration + NMOC Intercept (11)

where

NMOC Response = Analyzer's NMOC channel's reading in recording device units (see note following step 8).

NMOC Slope = Regression slope in recording device units per ppmC.

NMOC Concentration = Calibrated NMOC concentration in ppmC.

NMOC Intercept = Regression intercept in recording device units.

Post the NMOC channel's multipoint calibration curve equation on the analyzer's recording device and on Tables 5 and 11.

14. Record all operational parameter readings. These readings will now become the reference readings until another multipoint calibration is performed. Be certain that the station logbook, strip charts, etc., are properly annotated, dated, and initialed.

15. If level 2 zero and span checks are to be used, carry out such a check now to establish reference zero and span readings for subsequent comparison. (See section 2.0.9.1.3 of reference 10 for definitions and additional information for level 1 and 2 zero and span checks.)

5.6.2 Level 1 Zero and Span Check

The following level 1 zero/span procedure (2-point calibration) is similar to a multipoint calibration except that only the zero air standard and one upscale standard are used. These responses are then used to calculate the new calibration curves, which are used to correct subsequent monitoring data until another level 1 zero/span check or multipoint calibration is performed.

1. Follow the procedures in section 5.6.1, modified as follows.

   (a) Record responses on Tables 6 and 11.

   (b) After step 5, determine the zero drift in the CH_4, TOC, and NMOC channels (see section 3.8).

   If drift exceeds about $\pm$ 3%, perform step 6 and make the adjustments. If drift is less than about $\pm$ 3%, skip step 6.

   (c) After step 7, determine the span drift in the CH_4 and TOC channels (see Equation 4 in section 3.8). If drift exceeds about $\pm$ 7%, make the adjustments in steps 8 and 9.

(d) Omit step 11, but determine the slope and intercept of the CH_4 and TOC channel's level 1 calibration curve.

Post the level 1 calibration curves on Tables 6 and 11 and on the analyzer's recording device.

(e) After step 11, determine the span drift in the NMOC channel (see Equation 4 in section 3.8). If drift exceeds about $\pm$ 7%, make the adjustment in step 12.

(f) Omit step 13, but determine the slope and intercept of the NMOC channel's level 1 calibration curve. Post the level 1 calibration curve on Tables 6 and 11 and on the analyzer's recording device.

5.7 TROUBLESHOOTING

The manufacturer's instruction manual covers this subject under the same heading. Additional comments follow.

5.7.1 Preliminary Investigations

Operational problems, such as slow response to standards, inability to balance the TOC and CH_4 channels' responses, long stabilization periods, frequent flame-outs, or low sensitivity indicate the potential need for in-depth troubleshooting. Prior to undertaking in-depth troubleshooting procedures, a preliminary investigation is recommended to rule out variations in operational parameters.

1. Ensure that all pressure gauges on the analyzer are set to the specifications stated on the Manufacturer's Final Data Sheet. (If a manufacturer's data sheet is not available, use the instruction manual's settings.) If the analyzer has been operating properly for several months, ensure that pressure gauges are set to the readings recorded during the most recent multipoint calibration when analyzer operation was satisfactory.

2. Inspect the hydrogen source and hydrogen filters (located outside the analyzer) for proper operation.

3. Inspect the sample filter and replace if dirty. Replace the sample line leading to the analyzer if particulate buildup is noticeable.

4. Run a chromatogram as explained in section 5.7.2. If the chromatogram has changed since the last multipoint calibration, measure all flow rates in the analyzer and adjust to the proper specifications. Significant changes in flow may indicate a leak or an obstruction. If flow rates are within specifications, the gate timing may need adjustment.

5.7.2 Chromatogram Investigation

5.7.2.1 Procedures for Obtaining a Chromatogram--

NOTE: IF YOUR ANALYZER INCORPORATES THE "CALIFORNIA" MODIFICATION, SEE SECTION 5.3.4.

1. Allow the analyzer to sample an atmosphere containing a methane-in-air standard. Ensure that the atmosphere contains ambient levels of oxygen and that it is delivered at atmospheric pressure to the SAMPLE inlet of the analyzer (section 3.5).

2. Place the METER selector switch on the front panel to the ELECTROMETER position.

3. Connect a strip chart recorder to the analyzer's front panel. Select a fast chart speed that will allow easy identification of time on the strip chart.

4. Allow the analyzer to operate for about 10 minutes. Identify the repetitive measurement cycles which last 200 seconds. Each cycle should contain an automatic zero, CH_4 peak, automatic zero, and TOC peak. The strip chart recording of the cycle is a chromatogram. (See Figure 7 for a chromatogram depicting proper analyzer operation.)

5. Place the METER selector switch to the TIMER POSITION.

6. Advance the strip chart to a point where the pen can rest on a timing line of the chart. Stop the chart advance motor.

7. Observe the FRONT PANEL METER. Immediately after the meter indicates completion of a 200-second cycle (the needle will pass full scale then drop to zero), simultaneously place the METER selector to ELECTROMETER and engage the strip chart advance motor.

8. Observe the CH_4, TOC, and zero function lights. When the ZERO light illuminates, flick the chart recorder pen to mark the chart. When the light goes off, flick the pen again.

9. When the CH_4 light illuminates, flick the pen, and repeat when the light goes off.

10. Perform similar actions when the auto zero and THC lights illuminate and go off.

11. Remove the chart, measure the number of seconds from the start of the measurement cycle to each flick, and record the times on the chart.

12. For increased accuracy, repeat steps 6 through 11 several times and average the ON/OFF times for each gate. Also for increased accuracy, the same procedure can be repeated with a stopwatch instead of a strip chart. With the METER in the TIMER position, begin the watch when the cycle begins and call out times to an assistant when the function lights illuminate and go off. A digital watch with split time functions would be very helpful in performing this procedure.

5.7.2.2 Chromatogram Evaluation--

Chromatograms depicting proper and improper analyzer operation are shown in Figures 7 and 8. The chromatogram depicting proper operation shows auto zero gates ON and OFF just prior to the CH_4 and TOC peaks, the peak gates ON just prior to elution of the peak, and the peak gates OFF just after the response returns to the baseline.

Gate timing is critical because when a peak gate is ON, the signal from the FID is collected until the gate goes off. This signal is referenced to the auto zero signal and is eventually directed out the back panel to the recorder. If gate ON/OFF activity occurs during peak emergence, as in Figure 8, some of the peak may be missed. This results in an incorrect analyzer response for the component measured. A procedure to correct improper timing is discussed in 5.7.2.3, below.

Another characteristic of proper operation is a stable baseline response. The auto zero response prior to the CH_4 peak must be equal to the auto zero response prior to the TOC peak. In Figure 7, the responses during auto zeros remain the same, whereas in Figure 8, the responses during auto zeros are different. Variable baselines can be caused by differences in carrier flow rates when passing through the analytical column and when bypassing this column. The variable carrier flow rate will alter the hydrogen-to-carrier ratio, and thus alter the sensitivity of the FID. To prevent a change in sensitivity, the carrier flow rate bypassing the column during the TOC measurement must be balanced to the carrier flow rate passing through the column during the CH_4 measurement. A procedure to correct improper carrier flow rates is discussed in 5.7.2.3, below.

5.7.2.3 Adjustments to Correct Improper Baseline Shift on Gate Timing--

If evaluation of a chromatogram indicates improper carrier flow rates (discussed in 5.7.2.2) perform the following steps:

1. Place the front panel VALVE 1 and 2 switches in the OFF position and activate the AUTO H_2 SHUT OFF.

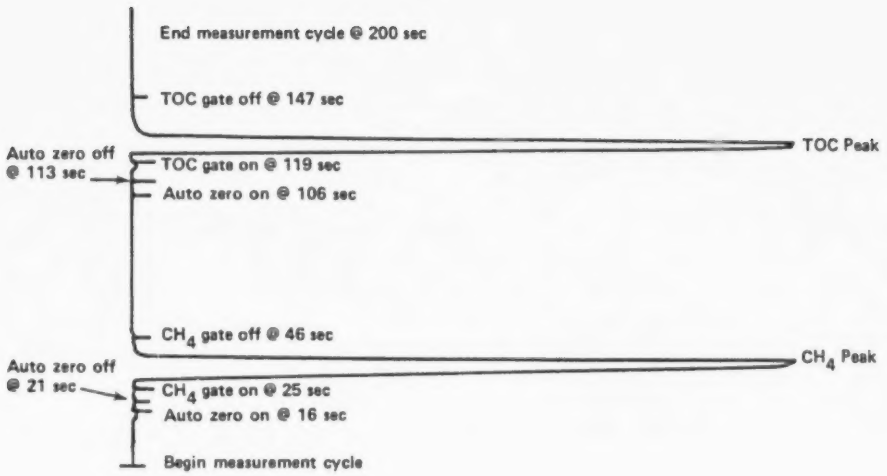
End measurement cycle @ 200 sec
TOC gate off @ 147 sec
TOC Peak
Auto zero off
@ 113 sec
TOC gate on @ 119 sec
Auto zero on @ 106 sec
CH4 gate off @ 46 sec
CH4 Peak
Auto zero off
@ 21 sec
CH4 gate on @ 25 sec
Auto zero on @ 16 sec
Begin measurement cycle

Figure 7. Chromatogram from a Bendix 8202 analyzer showing proper analyzer operation.

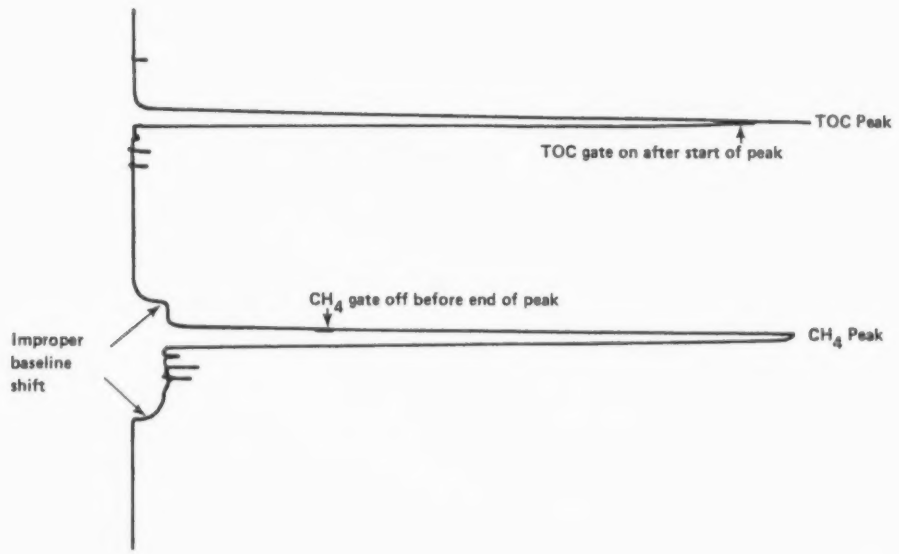

Figure 8. Chromatogram from a Bendix 8202 analyzer showing improper gate timing and baseline shift.

2. Connect a flow measuring device to the FID VENT on the back panel and measure the flow rate. Record this as the column flow rate. (The manufacturer may call this the "total column flow rate".)

3. Adjust the AIR CARRIER pressure regulator to obtain the column flow rate recorded on the Manufacturer's Final Data Sheet.

4. Connect a rotameter or mass flow meter to the FID VENT (if not already connected) and record the flow rate reading.

5. Place the VALVE 2 switch in the ON position and adjust the restrictor on Valve 2 (located inside the analyzer oven off port 4) to obtain the same flow rate as in step 4. The carrier flow bypassing the column should now be equal to the carrier flow through the column.

6. Activate the AUTO IGNITION switch, place both VALVE 1 and 2 switches in the AUTO position, and obtain a chromatogram.

7. If auto zero responses are not equal, adjust the restrictor on Valve 2 until auto zero responses are equal.

8. Activate the AUTO H_2 SHUT OFF and place VALVE 1 in the OFF position and VALVE 2 in the ON position. Measure the FID VENT flow rate. If this column bypass flow rate is not within $\pm$ 1% of the column flow rate obtained in step 3, troubleshoot the flow systems for leaks, obstructions, and column contamination.

If evaluation of a chromatogram indicated improper gate timing (discussed in 5.7.2.2), perform the following steps:

1. Operators of the 8201 model should refer to section 5.4.4 TIMING TROUBLESHOOTING in their instruction manual and Figure 7-16 COMPARATOR CARD SCHEMATIC DIAGRAM. Operators of the 8202 model should refer to section 5.5 CARD ADJUSTMENTS in their instruction manual and Figures 5-7, 5-8 and 5-9. Actions recommended in the instruction manual may be necessary if the following steps are unsuccessful in correcting improper gate timing.

2. Convert the ON/OFF times (obtained in the TAD section 5.7.2.1) for each improperly timed gate from seconds to timer-dial settings. The timer-dial (part #R-60) is a 10-turn, 200-second potentiometer that facilitates checking or setting the analyzer's gates. The timer-dial is mounted inside the 8201 analyzer beside the oven and is labeled TIMER POSITION. On the 8202 model, the timer-dial is mounted on the front panel and is labeled MANUAL CYCLE POSITION TIMER. For this discussion, the R-60 dial will be referred to in both models as the timer-dial.

In Figure 8, the improperly timed CH_4 gate goes off at X seconds. To convert seconds to timer-dial units, use the following equation:

$$\frac{X \text{ sec}}{200 \text{ sec}} \times 1000 \text{ timer-dial units} = y \text{ timer-dial units} \qquad (12)$$

3. Verify that the CH_4 gate indicator goes off at y timer-dial units. Place Valves 1 and 2 in the OFF position and the TIMER toggle switch in MANUAL. Increasing the timer-dial to past y units should cause the CH_4 gate indicator to go off.

4. The correct gate OFF time for the CH_4 peak should be several seconds after the peak returns to the baseline. Estimate the number of seconds that should be added to X to produce the correct OFF time. Convert this corrected time from seconds to timer-dial units and rotate the timer-dial to the corrected units. The CH_4 gate indicator should be off.

5. Locate Comparator Card #1 (component card J-10) inside the analyzer and rotate pot R-76 until the CH_4 gate indicator just comes on. Check gate operation by rotating the time dial through y units.

6. Reset the analyzer controls to obtain a chromatogram and verify that the CH_4 off gate is properly adjusted.

After the operator is confident performing timing adjustments, the verifying chromatogram need not be obtained until all timing adjustments are completed. For example, to correct the TOC ON gate problem in Figure 8, the Auto Zero ON and OFF gates may need to be adjusted to allow sufficient time for TOC gate adjustment. Follow the sequence of events discussed in steps 2 through 5, with modifications to fit the specific timing adjustment. Table 12 lists the specific potentiometers that will alter the different functions.

TABLE 12. COMPARATOR* CARD 1 (COMPONENT CARD J-10) FUNCTIONS AND POTENTIOMETER CONTROLS

Function	Potentiometer Number
CH_4 gate ON	R-66
CH_4 gate OFF	R-~~37~~ 76
TOC gate ON	R-54
TOC gate OFF	R-64
CH_4 Auto Zero ON	R-40
CH_4 Auto Zero OFF	R-52
TOC Auto Zero ON	R-29
TOC Auto Zero OFF	R-38

*Comparator card 2 (component card J-11) is identical to card 1 (J-10) but controls valve 1 and 2 ON/OFF timing and the actual timer cycle. See illustrations of these cards in the instruction manual for details.

5.7.2.4 Chromatograms Showing Analyzer Malfunctions--

The following section identifies specific chromatogram patterns, shown in Figure 9, that indicate analyzer malfunctions. The information is reproduced from the Bendix 8202 Reactive Hydrocarbon Analyzer Operation and Service Manual. Permission for reproduction was granted by the Bendix Corporation, Environmental and Process Instruments Division, Lewisburg, West Virginia 24901.

A. SYMPTOM: Constant basline drift in one direction, then starts in other direction.

PROBABLE CAUSE	REMEDIAL ACTION
Column has stopped bleeding and has started to clean.	Allow time for column to complete its cleanup.
Dirty carrier or dryer. Dirty dryer on H_2 and/or air on FID.	Change carrier bottle and/or dryers.
Dirty FID cell.	Clean FID cell.

B. SYMPTOM: Blip in baseline that varies with flow rate. The higher the flow, the larger the blip.

PROBABLE CAUSE	REMEDIAL ACTION
Dust in the FID cell.	Clean the cell.
Condensate in cell vent.	Clean the vent.
Varying pressure on FID vent.	Check for partial blockage. Also, room pressure may be changing due to doors or windows being opened.

C. SYMPTOM: No peaks.

PROBABLE CAUSE	REMEDIAL ACTION
Electrometer off.	Check jet potential voltage. Turn power ON.
No carrier gas flow.	Check carrier gas supply and carrier shut-off switch.
No flame.	Check H_2 and air flows and light flame.

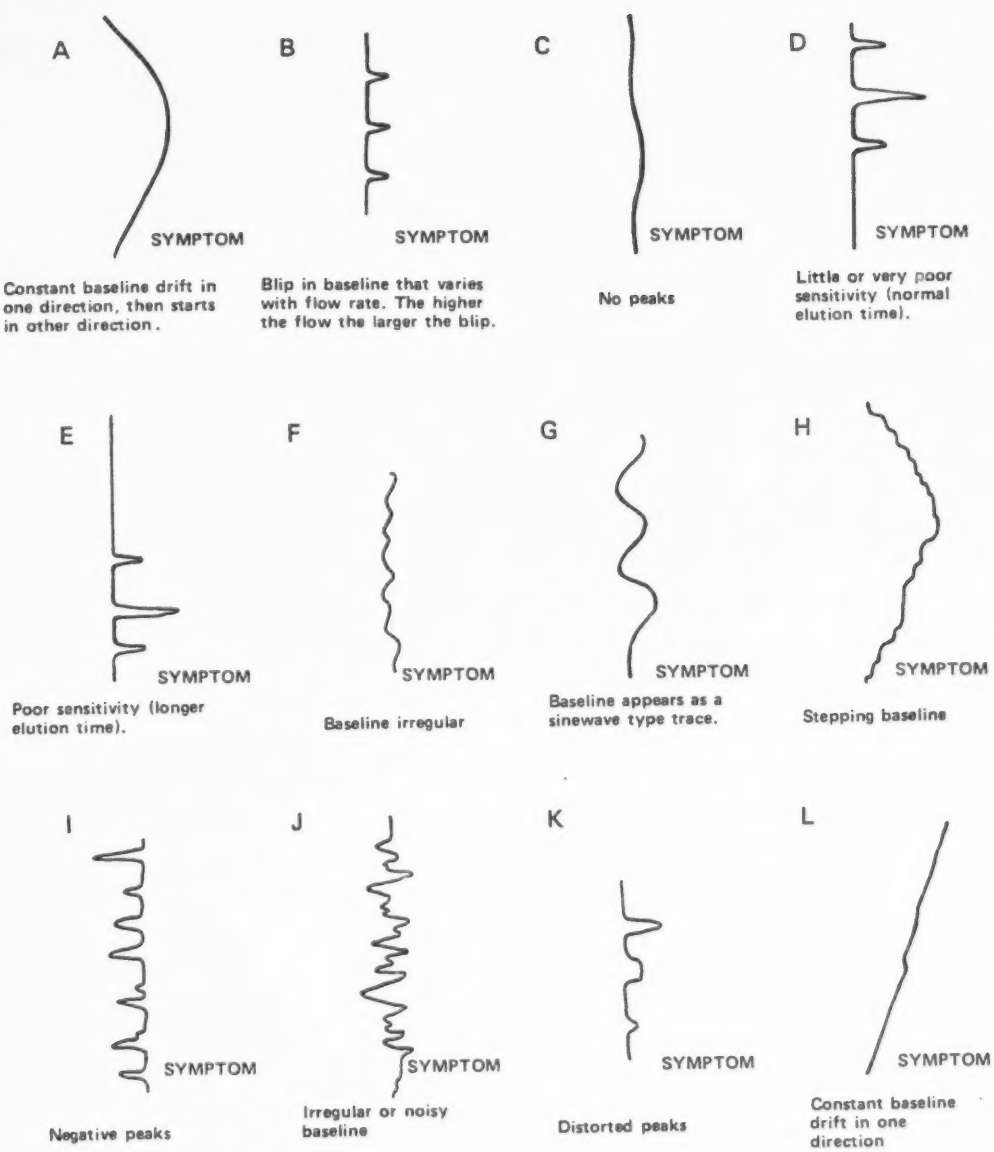

Figure 9. Chromatograms showing analyzer malfunctions.

Defective recorder.	Refer to recorder manual for troubleshooting procedure.
Leak at column connections.	Tighten connections.
Recorder not connected correctly.	Refer to schematic of recorder hookup. Be sure no jumpers are grounding signal.
No voltage applied to detector cell on ionization detector.	Check electrometer voltage output. Refer to electrometer schematic.
Cable disconnected from FID.	Connect the cable.
Column temperature too low to elute peaks.	Raise column temperature to proper level.

D. SYMPTOM: Little or very poor sensitivity (elution time normal).

PROBABLE CAUSE	REMEDIAL ACTION
Incorrect sample size.	Clean sample chamber.
Electrometer OFF (FID).	Turn electrometer ON.
No sample flow.	Check pump operation and STANDARD SAMPLE solenoid (SOLV 3) valve operation.

E. SYMPTOM: Poor sensitivity (longer elution time).

PROBABLE CAUSE	REMEDIAL ACTION
Analyzer temperature too low.	Check and reset to correct temperature.
Carrier flow too low.	Increase flow rate.
Leak downstream of injection valve.	Locate and repair leak.

F. SYMPTOM: Baseline irregular.

PROBABLE CAUSE	REMEDIAL ACTION
Column bleeding.	Replace defective column with a properly conditioned column.

FID cell contaminated.	Clean the FID cell.
Bad electrical ground.	Check the analyzer for proper grounds.
Carrier gas regulation poor.	Check carrier gas flow control and regulator. Be sure upstream pressure is high enough to operate regulator. Pressure should be at least 10 psig.
Defective electrometer.	Check electrometer.
Unstable oven temperature.	Check to see if temperature controller is operating properly.
H_2 and/or air regulation poor.	Check flow rates to be sure of proper flows and regulation.

G. SYMPTOM: Baseline appears as a sinewave type trace.

PROBABLE CAUSE	REMEDIAL ACTION
Poor temperature control.	Check the temperature control for proper operation. Check seal around door for leaks. Be sure there is no obstruction to air flow in the oven.
Hydrogen flow too high.	Lower the hydrogen flow.
Dryers dirty.	Replace the dryers.
Leak at jet.	Locate and repair leak.
Low tank pressure on carrier gas--bottle pressure should be over 10 psig.	Replace tank.
Defective carrier gas flow regulator.	Replace the flow regulator.
Defective H_2 and/or air regulators.	Clean or replace regulator.

H. SYMPTOM: Stepping baseline.

PROBABLE CAUSE	REMEDIAL ACTION
Defective recorder.	Refer to the recorder manual.

I. SYMPTOM: Negative peaks.

PROBABLE CAUSE	REMEDIAL ACTION
Signal reverse circuit energized.	Refer to Control Module manual (if applicable).
Recorder leads reversed.	Reverse the recorder leads on the rear hookup panel.

J. SYMPTOM: Irregular or noisy baseline.

PROBABLE CAUSE	REMEDIAL ACTION
Loose leads.	Tighten all leads from power supply to cell.
Bad ground connections.	Tighten all ground connections to ensure earth potential.
Carrier gas leak.	Locate and repair leak.
Contaminated columns.	Replace or recondition columns.
Contaminated carrier gas.	Replace carrier gas bottle and replace dryers and filters.
Dirty switch or switches.	Locate the dirty switch and clean with suitable solvent.
Recorder slidewire dirty.	Clean with suitable solvent.
H_2 and/or air flow rates too high or too low.	Adjust flow rates.
Detector insulators dirty.	Clean insulators.
Contaminated FID cell.	Clean FID cell.

Detector coaxial cable defective.	Replace the coaxial cable.
Loose signal leads.	Check all connections to be sure they are tight.

K. SYMPTOM: Distorted peaks.

PROBABLE CAUSE	REMEDIAL ACTION
Flame burning above jet into ignitor or collector electrode area.	Hydrogen and air flows too high. Reduce flows.

L. SYMPTOM: Constant baseline drift.

PROBABLE CAUSE	REMEDIAL ACTION
Column bleed.	Replace or recondition columns.
Dirty carrier.	Replace carrier or dryer, and filters.
Dirty FID cell.	Clean FID cell.
Defective electrometer.	Repair or replace electrometer.
Detector temperature increasing.	Allow time for detector temperature to stabilize.
Leak in column tubing.	Locate and repair leak.
Column temperature too high for the column.	Lower the column temperature or choose another type of column.

5.7.3 Sample and Back-Flush Valve Leak Check

1. A pressure test apparatus described in section 2.4.2 can be used. The analyzer's instruction manual also addresses leak-checks.
2. Select the CALIBRATE position on the front panel toggle switch.
3. Cap the SAMPLE VENT.
4. Pressurize the CALIBRATE inlet port. With VALVE 1 in the ON position, pressure decay indicates a possible leak in the sample valve at O-rings

to ports 3, 5, 4, and 6. With VALVE 1 in the OFF position, pressure decay indicates a possible leak in the sample valve at O-rings to ports 3, 2, 1, and 6.

5. Remove the cap and pressure source.

6. Cap the FID vent and the back-flush vent.

7. Pressurize the AIR CARRIER inlet port. When VALVE 2 is in the ON position (and VALVE 1 is known to be leak proof), pressure decay indicates a possible leak in the back-flush valve at O-rings to ports 3, 5, 4, and 6. With VALVE 2 in the OFF position, pressure decay indicates a possible leak in the back-flush valve at O-rings to ports 3, 2, 1, and 6.

SECTION 6

AUGMENTED PROCEDURES FOR THE BECKMAN 6800 AIR QUALITY CHROMATOGRAPH (CH_4, TOC, NMOC)

NOTE: READING SECTIONS 1, 2, AND 3 BEFORE SECTION 6 IS STRONGLY RECOMMENDED. INFORMATION WHICH IS CRITICAL TO THE UNDERSTANDING AND SUBSEQUENT ACCURATE OPERATION OF THIS ANALYZER IS DETAILED IN THOSE SECTIONS AND WILL NOT BE REPEATED HERE.

The manufacturer has prepared a relatively detailed instruction manual which can guide users during installation and operation of the model 6800 analyzer. The thoroughness of the manual will therefore allow this section to be brief. As stated in the introduction, the purpose of this TAD is to supplement the analyzer's instruction manual by augmenting critical installation and operation procedures.

6.1 PRINCIPLES OF OPERATION

The analyzer's instruction manual contains a discussion of this subject under "Instrument Theory". A brief summary of the CH_4, TOC, and NMOC component analysis follows.

A measured amount of sample is injected directly into the FID to measure TOC concentrations. Following the TOC measurement, a second, separate sample is injected into a stripper column to separate CH_4 and CO from CO_2 and heavy organics. A second column then separates CH_4 from CO prior to injection into the FID, where the CH_4 concentration is measured. The CH_4 concentration can then be externally subtracted from the TOC concentration to obtain a measure of the NMOC concentration. (Modifications are available to enable internal subtraction of CH_4 from TOC to obtain a direct NMOC output.)

6.2 SYSTEM DESCRIPTION

A detailed description of the analyzer is given in the analzer's instruction manual. This TAD will therefore not address location of components, but will emphasize the uses and precautions of those which are critical.

6.2.1 Flame Ionization Detector

The analyzer contains one FID. Response from the CH_4 and TOC channels must be balanced to a methane-in-air standard. If zero air is necessary to dilute span gas to the required calibration concentrations, the CH_4 and TOC channels must first be balanced to the zero air standard, and then to the methane-in-air standard.

6.2.2 Hydrogen Pressure Gauge

The flow of hydrogen fuel to the FID is controlled by a pressure regulator, gauge, and restrictor. Increasing the pressure reading on the hydrogen gauge will increase the flow of hydrogen to the FID and affect the sensitivity of the burner. Ensure that the hydrogen reading does not vary from day to day. If the reading does vary, measure the flow rate and take appropriate corrective actions.

CAUTION: ENSURE THAT ALL TUBING CARRYING HYDROGEN GAS IS LEAK PROOF. SEE INSTRUCTION MANUAL, PAGE 12.

6.2.3 Flame-out Indicator

In the event of a flame-out, the flame-out indicator will illuminate. If the status of the flame is in doubt, observe analyzer response first to zero air, and then to a sample known to contain methane. If the TOC channel's responses are the same to both samples, the flame is out.

6.2.4 Slider Valves

The slider valve is a stainless steel valve which contains a Teflon® slider. The ON/OFF positions of the slider dictate where sample is directed. Friction of the slider against the stainless steel causes wear of both the slider and the steel, ultimately resulting in a leak. Frequent maintenance of these valves is strongly recommended. The slider should be replaced every 6 months, or sooner if a leak develops or if the slider begins to open and close sluggishly. When the slider is replaced, the stainless steel valve must be lapped to ensure a smooth seat for the slider. During reassembly, the valve connectors must be tightened uniformly and only to the point where no sample leakage occurs. Use of a vacuum applied to a valve port is recommended to aid in determining when the valve is leak-proof and thus sufficiently secure.

6.2.5 Columns

To prevent column contamination, all columns should be capped whenever they are removed from the analyzer or whenever the analyzer is powered-down

for an extended period of time. Failure to do so will allow the molecular sieve to absorb CO_2. Subsequent operation results in CO_2 outgassing which will show up as a noisy, erratic baseline response.

6.3 MODIFICATIONS

The model 6800 analyzer has been slightly modified over the years. The principles of operation and detection have not changed, but the following modifications have been adopted.

6.3.1 Stripper Column

To improve stability of the molecular sieve column (which separates CO from CH_4), the stripper column that preceeds the molecular sieve column has been modified. The original packing material, Poropak, appeared to break down and allow passage of volatile fragments to the sieve column, resulting in deactivation. To correct this, a combination column containing silica gel and an inert Teflon® support/partition liquid has replaced the Poropak column.

6.3.2 Hydrogen Pressure Regulator

To eliminate diffusion of atmospheric water vapor into the hydrogen carrier stream, the original permeable diaphragm located in the hydrogen carrier gas regulator has been replaced with a stainless steel diaphram. Also, the body of the regulator has been changed to brass.

6.3.3 Scrubber

The scrubber (683526) upstream of the molecular sieve column is not necessary and has been removed. Subsequent resizing of the capillary to adjust pressures and flows must be performed when the scrubber is removed.

6.3.4 Sample Pump

In the normal configuration of the sample pump, the sample passes through the pump before analysis by the analyzer. However, a very simple modification allows the pump to draw the sample through the sample loops in the analyzer such that the sample does not pass through the pump first. The modification consists of disconnecting the pump from its normal connection to the 3-way solenoid valve, and reconnecting it in series with the line going from Valve B to the SAMPLE VENT. The pump inlet is connected to port 6 of Valve B, and the outlet is connected to the SAMPLE VENT. The bypass is removed from the pump, and a needle valve, installed between the pump inlet and Valve B, is used to control the flow rate. The sample inlet for the analyzer then becomes the port on the 3-way solenoid valve to which the pump was originally connected.

6.3.5 Pressure Regulator

The service air, air carrier, hydrogen fuel, and burner air pressure regulators have been replaced by improved regulators (865774).

6.3.6 Catalytic Converter Board

The catalytic converter board installed in analyzers before February 1973 contains a 4.7-ohm resistor (R1) rated at 2 W. This should be replaced with a 5-ohm 5-W resistor.

6.3.7 Oxidation Catalyst

The oxidation catalyst, which scrubs air to be used for combustion and sample carrier, has been replaced. The original nickel oxide catalyst has been replaced with palladium-on-alumina.

6.4 INSTALLATION

The analyzer's instruction manual contains a discussion of this subject under the same heading. Additional comments and a specific start-up procedure follow.

6.4.1 General Comments

1. Before supplying power to the analyzer, ensure that all electronic component cards are properly seated by attempting to push the cards snugly into the connectors.

2. Minimize the distance between the analyzer and the sample manifold. Use clean 3 mm (1/8-in) diameter inert tubing as the sample line. The sample line length should not exceed 3 m (10 ft).

3. Leak-checks should be made on the hydrogen, air carrier, and sample flow systems of old and new analyzers. See sections 3.1.4 through 3.1.6 in the instruction manual for details. A leak-check apparatus is discussed in section 2.4.2 of this TAD.

CAUTION: ONLY EXPERIENCED, QUALIFIED OPERATORS SHOULD PERFORM THE LEAK-CHECK. AVOID FINGER CONTACT WITH THE FITTING THREADS DUE TO POSSIBLE TRANSFER OF OILS THAT WILL TEMPORARILY INCREASE THE BASELINE RESPONSE.

4. Hydrogen gas, burner air, and carrier air should not contain TOC contaminant concentrations that cannot be "bucked-out" by the auto zero. Perform a level 1 zero and span check after replacing any of these support gases.

5. Zero air used to dilute span gases must not contain more than 0.1 ppmC TOC concentration.

6. Connect recorders to the CH_4 and TOC outputs (and NMOC output if available) located on the rear panel connector. Also, a temporary recorder for the front panel jack (to record chromatograms) is useful.

7. Calibration gases should enter the analyzer through the SAMPLE inlet port. Do not connect calibration gas to the CALIBRATE port.

6.5 OPERATION

6.5.1 Start-up

1. Prior to start-up and operation, the operator should have a thorough understanding of the flow diagrams and should know the location and function of the system controls.

2. Turn off all gases except service air.

3. Set electrical power switches:

   (a) Front-panel Power Switch, ON

   (b) Rear-panel Pump Switch, OFF

   (c) Rear-panel Power Switch, ON

   The catalytic heater and oven heater indicators should illuminate. After 30-45 minutes, the oven heater indicator should flash on and off intermittently, indicating operating temperatures have been reached.

   (d) Verify that either the Reset or the Start switch/indicator is lit.

4. Check for proper functioning of slider valves.

   (a) Move Manual/Auto switch to Manual and Calibrate/Operate switch to Operate.

   (b) Turn on Flame-out override switch. Turn off all other manual function switches.

   (c) Open oven door to permit visual check of slider valve operation. Momentarily close Start switch. Turn on Valve A switch and observe slider movement and illumination of switch indicator. Sluggish movement indicates problems.

(d) Turn on Valve B switch and observe slider movement and illumination of switch indicator.

(e) Move Manual/Auto switch to Auto, Valves A and B should deactivate and indicators should go out.

(f) Return valve switches A and B to off position and Manual/Auto switch to Manual.

5. Leak-check the air and sample flow systems as described in section 3.1.5 and 3.1.6 of the analyzer's instruction manual.

> WARNING: CHECK THE CONDITION OF THE WATER DRAIN TUBING BETWEEN THE FID AND OVEN EXTERIOR FOR HARDENING AND BRITTLENESS. LEAKS IN THIS DRAIN MAY LEAD TO AN EXPLOSION BY ALLOWING A BUILDUP OF HYDROGEN IN THE OVEN DURING REPEATED IGNITION ATTEMPTS.

6. Establish correct gas flows.

(a) Turn off H_2 fuel at the pressure control.

(b) Connect a flow meter to the hydrogen carrier and fuel line after disconnecting from FID. (See Figure 5-9 in the instruction manual.)

(c) Adjust H_2 Carrier pressure control to obtain 25 cm^3/min and record gauge reading. A typical reading is between 12 and 20 psig.

(d) Adjust H_2 Fuel pressure control to obtain a total flow (carrier plus fuel) of 30 to 31 cm^3/min, and record gauge reading. A typical gauge reading is between 5 and 11 psig.

(e) Disconnect flow meter and reconnect H_2 carrier and fuel line.

(f) Connect a flow meter to the air carrier line after disconnecting from the FID.

(g) Adjust air carrier pressure control to obtain a carrier flow of 33 to 35 cm^3/min and record the gauge reading. A typical gauge reading is 18-26 psig. Disconnect the flow meter and reconnect the tubing.

7. Ignite detector burner.

   (a) Place Flame-Out Override switch to ON.

   (b) Place the Manual Range Select switch to 10 and the Monitor Select switch to Ampl. Out. Note the meter response while proceeding with the following steps.

   (c) Reduce the Burner Air pressure gauge setting by approximately 50% and momentarily (3 to 5 seconds) raise the Flame Ignition switch. The meter response should drive upscale momentarily upon ignition of the flame, then settle to some upscale level, indicating flame ignition.

   (d) Repeat the above step until flame ignites, and then reset burner air to recorded setting.

   (e) Turn off Flame-Out Override switch.

8. Allow system to stabilize 12 to 24 hours prior to performing any calibrations.

6.5.2 Periodic Calibrations and Zero/Span Checks

An initial multipoint calibration is recommended to verify linearity in the calibration curve. Periodic level 1 zero and span checks are thereafter necessary to update the calibration curve. The frequency of level 1 zero and span checks and subsequent multipoint calibrations should be based on the analyzer's performance. Performance can be monitored through the use of a control chart which documents responses to standards, and ultimately enables calculation of variation in response to standards (drift). (See section 2.0.9 of reference 10 for details on calibrations and level 1 and level 2 zero and span checks. See section H of reference 14 for details on control charts. See section 6.6 of this TAD for specific calibration procedures.)

6.5.3 Operational Checks

The analyzer's operational parameters should be checked at least once a week, or more frequently if necessary. Parameters that should be routinely checked and recorded on Table 13 are pressure gauge readings, analyzer responses, and other routine checks that may be necessary. (Routine monitoring may not require that unadjusted responses to standards be recorded; however, special cases may warrant such data.) If any of these parameters shows substantial change from the last check, or if drift out of the specified range has occurred, recheck the analyzer calibration with a level 1 zero and span check and make necessary corrections.

TABLE 13. FORM FOR RECORDING ROUTINE OPERATIONAL DATA FROM THE BECKMAN 6800 NMOC ANALYZER

Day	Zero Response						Span Response						Span Gas / Conc.	% Diff.			Pressure Gauges					Recorder Zero				
	Unadjusted			Adjusted			Unadjusted			Adjusted								Air								
	TOC	CH_4	NMOC	TOC	CH_4	NMOC	TOC	CH_4	NMOC	TOC	CH_4	NMOC		TOC	CH_4	NMOC	H_2 Fuel	Burner	Carrier	Service	H_2 Carrier	TOC	CH_4	NMOC	Chromat	

MONTH:

6.5.4 Routine Chromatograms

A chromatogram should be evaluated during start-up, and on a weekly basis thereafter, to determine if analyzer parameters have shifted outside the limits of proper operation. Critical parameters, such as gate timing, FID sensitivity, and flow rates can be investigated through a careful evaluation of the chromatogram. The procedure for obtaining a chromatogram and setting gate timing follows.

1. Momentarily close RESET switch to place system in reset condition.

2. Set OPERATIONAL STATUS switches as follows.

   (a) Move Manual/Auto Switch to Manual.

   (b) Move Calibrate/Operate Switch to Operate.

   (c) Move Manual ATT/Auto ATT Switch to Manual ATT.

3. Turn off front panel switches designated Valve A, Valve B.

4. Allow the analyzer to sample an atmosphere containing a methane-in-air standard at about 8 ppmC plus about 10 ppm or higher CO. Ensure that the atmosphere contains ambient levels of oxygen and that it is delivered at atmospheric pressure to the SAMPLE inlet of the analyzer (section 3.5).

5. Move Monitor Select Switch to Ampl. Out.

6. Momentarily close Start switch and turn Manual Range Select switch to 1.

7. Turn on Auto Zero switch until meter reading drops to zero, then turn switch off. If zero is not obtained, refer to section 6.5 in the analyzer's instruction manual.

8. Turn Manual Range Select switch to 100 and Chromatogram Attenuator switch to 1 for a span gas between 8 and 10 ppm.

9. Turn on chromatograph recorder chart drive. Select a chart speed that permits adequate peak separation. The minimum chart speed should be 40 cm/hr (16 in/hr).

10. One or more manual test chromatograms, using the recorder connected to the front panel jack, must now be run to determine TOC peak emergence time. To inject the sample, turn on the Valve B switch for 25 seconds. The recorder should register a flat-topped peak. If the peak is off-scale, turn the chromatogram attenuator switch to the next higher

setting, wait at least 30 seconds, then repeat actuation of Valve B switch. Continue until desired onscale peak is obtained. When onscale peak height is obtained, note and record settings used on Manual Range Select and Chromatogram Attenuator switches. Also note the times of the start and end of the TOC peak.

NOTE: ALLOW AT LEAST 30 SECONDS BETWEEN SUCCESSIVE SAMPLE INJECTIONS WITH VALVE B TO ENSURE COMPLETE PURGING OF THE SAMPLE LOOP.

11. A series of two-component manual test chromatograms must now be run to determine the methane and carbon monoxide peak emergence times and Valve A actuation time. Both CH_4 and CO components must be run, even through some users may not require the CO measurement output. It has been determined that column degradation can cause overlapping of the CO and CH_4 components. Therefore, the CO may act as an interferent for the CH_4 measurements. It is not sufficient to remove, turn off, or deprogram the CO component card to eliminate the interferent response.

    (a) In the first trial run, when the recorder pen is on a major time division on the chart, turn on Valve A. After 75 seconds, turn off Valve A switch and wait for the methane and carbon monoxide peaks to register on the recorder chart. If peaks are offscale, turn the chromatograpm attenuator switch to the next higher setting and repeat. Note the height of the methane peak.

    (b) In the next trial, turn on Valve A for 65 seconds and note the height of the methane peak on the resulting chromatogram.

    (c) Continue trial runs, each time using a shorter energization period (10-second decrement) for Valve A, until a chromatogram is obtained showing decreased amplitude for the methane peak. (Be sure to take into consideration any changes in the setting on the Crhomatogram Attenuator and Manual Range Select Switches). A decreased height of methane peak indicates premature de-energization of Valve A, with a resultant loss of a portion of the sample. Therefore, the correct energization period for Valve A is about 6 to 10 seconds longer than that used in the last trial run. For most instruments, duration of the required energization period is between 40 and 75 seconds.

(d) When the desired chromatogram is obtained, note and record the settings used on Manual Range Select and Chromatogram Attenuator Switches. Also note the start and end times of the CH_4 peak.

12. Using the test data obtained in the preceding steps, program the time-related functions for the Valve Board, auto zero board, and individual component boards following the procedures given in Section 3.0 of the analyzer's instruction manual.

NOTE: PRIOR TO REMOVING OR INSTALLING THE BOARDS FOR PROGRAMMING, TURN OFF THE ELECTRICAL POWER SWITCH LOCATED ON THE FRONT PANEL. IF THE SWITCH IS NOT PROMPTLY RESTORED TO THE ON POSITION, THE FAILSAFE FEATURES WILL TURN THE ANALYZER OFF.

13. Timing Circuit Board for Valves A and B.

(a) Program the Valve B Function, TOC sample injection "on" at 001 second, and "off" at 025 seconds.

(b) Program the Valve A, Sample-Injection/Stripper Function "on" at 030 seconds. The required "off" time is determined from the energization time determined in step 11 plus 30 seconds. For example, if the duration of the required energization period for Valve A has been determined to be 65 seconds, the corresponding "off" time would be 095 seconds, with respect to time "zero".

14. Component board assigned to TOC.

(a) Program the TOC component gate window to include the full TOC peak on the TOC test chromatogram. The typical timing is "on" at 006 seconds; "off" at 020 seconds. Leave the window "on" as long as possible to allow detection of heavy organics.

(b) Set range selector switch S3 for the 10 ppm range position.

15. Component board assigned to methane.

    (a) Program the "on" and "off" times to include the full methane peak on the methane manual test chromatogram (step 11). Remember to add 30 seconds to the times determined in step 11.

    (b) Set Range Select switch S3 for the 10 ppm range.

16. Auto Zero Board.

    (a) Program the first auto-zero "A" to occur 12 to 15 seconds prior to the emergence of the methane peak on a stable portion of the baseline. Duration of the auto zero period need only be 4 or 5 seconds. Check the manual test chromatogram (step 11) to verify flat baseline in the region, to be used for auto zeroing.

    (b) Program the second auto-zero "B" near the end of the cycle (292-298 seconds) where the baseline is flat (preparatory to the TOC peak on the next cycle). The auto-zero function must not be programmed to coincide with an elution of a peak.

17. Run additional chromatograms to verify the various time settings, if necessary.

6.6 CALIBRATION

This section details specific procedures for multipoint calibrations and zero and span checks of the Beckman 6800. The analyzer's instruction manual may contain deviations from these procedures, but the step-by-step procedures that follow are currently recommended by the EPA.

6.6.1 Multipoint Calibration

1. Disconnect the analyzer's sample line from the ambient sample manifold and reconnect it to the calibration system's manifold. Cap the port on the ambient manifold, and on any open ports on the calibration system's manifold.

2. Place the analyzer's range selector switch in the desired concentration range. (Calibrate the analyzer on the range normally used during ambient sampling.)

3. Supply an atmosphere of methane standard to the calibration manifold at a flow rate 20 to 50% greater than the analyzer's sample flow demand. DO NOT PRESSURIZE THE ANALYZER'S SAMPLE INLET.

4. Run a chromatogram (at least once a week) and evaluate it for proper analyzer operation (gate timing, flow rates, etc.; see section 6.5.3 for procedures). Investigate unusual behavior and consult trouble-shooting for procedures to correct the problems. Allow the analyzer to stablize before continuing calibration.

5. Supply an atmosphere of the zero standard to the sample manifold at a flow rate 20 to 50% greater than the analyzer's sample flow demand. DO NOT PRESSURIZE THE ANALYZER'S SAMPLE INLET. The test atmosphere must contain an ambient level of oxygen and must not contain more than 0.1 ppmC TOC. (See section 3.2 for details.)

NOTE: THE ANALYZER'S AUTO ZERO WILL CORRECT FOR MINOR CONTAMINATION IN THE HYDROGEN AND BURNER AIR BUT WILL NOT CORRECT FOR ZERO GAS CONTAMINATION. DISCREPANCY BETWEEN THE AUTO-ZERO LEVEL AND THE ZERO AIR RESPONSE MAY INDICATE CONTAMINATED ZERO AIR.

6. Set Operational status switches as follows.

   (a) Move Single/Continuous to Continuous.
   (b) Move Manual/Auto to Auto.
   (c) Move Calibrate/Operate to Operate.
   (d) Move ATT/Auto ATT to Auto ATT.

   Momentarily actuate the start switch and allow the analyzer to complete 3 complete cycles in the automatic mode, or to cycle until a stable response is obtained on the memory recorder outputs for each component.. Record the stable responses on Tables 5 and 13. If the responses are not within $\pm$ 1% of each other and zero, ensure that the TOC and CH_4 channel electronics are balanced before investigating contamination in the cylinder, lines, and regulators. (Be certain all regulators contain metallic diaphragms and are LOX cleaned.)

   If the analyzer does not contain an NMOC subtraction card, proceed to step 8.

7. Zero the NMOC response by the following procedure:

   (a) Set operational status switches as follows.

   Move Manual/Auto to Manual.
   Move Calibrate/Operate to Calibrate.

   (b) On the TOC component board, place the OFF/MANUAL/AUTO switch on MANUAL. Make certain this switch on the CH_4 component board is in either the OFF or AUTO position.

   (c) Place the MONITOR SELECT switch at the memory position assigned to TOC (usually MEMORY 1 position). Adjust CALIBRATE control for a reading of exactly zero on the front panel meter. Leave the CALIBRATE control at this setting until the zero procedure is completed.

   (d) On the NMOC subtraction board, remove the pin from the position marked SAME RANGE or LOWER RANGE, thus removing the CH_4 memory input from the subtraction board. Place the AUTO/MANUAL switch on MANUAL. Insert the pin into the connection marked READOUT MEMORY 5 POSITION. (With a five-component analysis system, the pin may be used only during initial zeroing of the subtraction circuit. The pin must be removed prior to programming of the component board assigned to the fifth component.)

   (e) Place MONITOR SELECT switch at MEMORY 5 position. Adjust potentiometer R14 on the subtraction board for a zero reading on the front panel meter.

   (f) Replace pin in the SAME RANGE or LOWER RANGE position.

   (g) Repeat step 6 and obtain the stable NMOC response to the zero standard. Record the response on Tables 5 and 13.

8. Supply an atmosphere of the methane standard to the calibration manifold at a flow rate 20 to 50% greater than the analyzer's sample flow demand. DO NOT PRESSURIZE THE ANALYZER'S SAMPLE INLET. The methane concentration should be between 70 and 90% full scale.

9. Set Operational status switches as follows.

   (a) Move Single/Continuous to Continuous.
   (b) Move Manual/Auto to Auto.
   (c) Move Calibrate/Operate to Operate.
   (d) Move Manual ATT/Auto ATT to Auto ATT.

10. Momentarily actuate the start switch and allow chromatograph to complete 3 complete cycles in the automatic mode, or to cycle until a stable response is obtained on the memory recorder outputs for each component. If the recorder output is offscale for a given component, turn the respective potentiometer (R12) two turns counterclockwise to decrease memory gain and repeat until an onscale response is obtained.

11. Calibrate the CH_4 channel as follows.

    (a) Momentarily actuate the reset switch.

    (b) Set operational status switches as follows.

        Move Manual/Auto to Manual.
        Move Calibrate/Operate to Calibrate.
        Move Manual ATT/Auto ATT to Auto ATT.

    (c) Turn Manual range select to position 1 and the CH_4 component board switch to the manual (center) position.

    (d) Adjust the calibrate control to simulate the memory recorder response of the CH_4 component which was obtained with the methane span gas.

    (e) Adjust the CH_4 component board potentiometer (R12) to yield the correct memory recorder response as calculated in the following equation:

$$\text{Response} = \frac{\text{Sample concentration}}{\text{URL}} \times \text{url} + \text{zero offset} \qquad (13)$$

where

Response = Response of the recording device measuring the analyzer output in recording device units.

Sample Concentration = Concentration of the calibration standard delivered to the analyzer in ppmC.

URL = The upper range limit of the analyzer in ppmC.

url = The upper range limit of the recording device in recording device units.

Zero offset = The amount the recording device response is set above the zero baseline while the analyzer is measuring the zero calibration standard (in recording device units).

NOTE: The response, url, and zero offset must be in identical units. For example, if a strip chart recorder is the recording device, units will be percentages of chart and the url may equal 100% chart. If a digital voltmeter (DVM) is the recording device, units may be millivolts or volts and the url may be, for example, 1000 mV. If a Data Acquisition System (DAS) is the recording device, units may be ppmC and the url will equal 10 ppmC. If the front panel meter on the analyzer is the recording device, units will be ppmC and the url may be 10 ppmC.

(f) Return the CH_4 component board switch to the auto position.

12. Calibrate the TOC component as follows.

(a) Momentarily actuate the reset switch.

(b) Set operational status switches as follows.

Move Manual/Auto to Manual.
Move Calibrate/Operate to Calibrate.
Move Manual ATT/Auto ATT to Auto ATT.

(c) Turn Manual range select to position 1 and the TOC component board switch to the manual (center) position.

(d) Adjust the calibrate control to simulate the memory recorder response of the TOC component which was obtained with the methane span gas.

(e) Adjust the TOC component board potentiometer (R12) to yield the correct memory recorder response as calculated in Equation 13. The CH_4 and TOC responses to the methane standard must be within ±1.0% of each other and the actual concentration of the test atmosphere.

(f) Return the TOC component board switch to the auto position.

13. Return all switches to the normal automated "run" position. Momentarily actuate the start switch and allow the chromatograph to complete 2 automated cycles to verify that adjustments were correct.

14. Determine the CH_4 and TOC channel's response to two or more additional concentrations of the methane standard, spaced approximately equally over the analyzer range. (The NMOC channel's response should remain equal to the earlier response for zero standard.) Record the CH_4 and TOC channel's responses (from the recording device) on Table 5. Using a calculator, perform a least squares linear regression of the CH_4

channel responses (to methane and zero standards) and the corresponding calibration concentrations. The calibration concentrations should be in units of ppmC and entered into the calculator as the independent variable X. The CH_4 channel's response should be in units of the recording device and entered as the dependent variable Y. A correlation coefficient (r) of 0.9996 or better verifies the CH_4 response is linear. (If the response is not linear, plot the data and determine if an error has been made in data entry or in determination of calibration concentration.) Obtain the slope and intercept of the regression and record the equation in the following form:

CH_4 Response = CH_4 Slope X Methane Concentration + CH_4 Intercept (14)

where

CH_4 Response = Analyzer's CH_4 channel reading in recording device units (see note following step 11).

CH_4 Slope = Regression slope in recording device units per ppmC.

Methane Concentration = Calibrated methane concentration in ppmC.

CH_4 Intercept = Regression intercept in recording device units.

Post the CH_4 channel's calibration curve equation on the analyzer's recording device and also on Tables 5 and 13. Also, using the above equation and the TOC responses, determine the TOC calibration curve, and post accordingly.

15. Supply an atmosphere of the propane standard to the calibration manifold at a flow rate 20 to 50% greater than the analyzer's sample flow demand. DO NOT PRESSURIZE THE ANALYZER'S SAMPLE INLET. The propane concentration should be between 70 and 90% full scale.

16. Set Operational status switches as follows.

    (a) Move Single/Continuous to Continuous.
    (b) Move Manual/Auto to Auto.
    (c) Move Calibrate/Operate to Operate.
    (d) Move Manual ATT/Auto ATT to Auto ATT.

    Momentarily actuate the start switch and allow chromatograph to complete 3 complete cycles in the automatic mode, or to cycle until a stable response is obtained on the memory recorder outputs for each component. The TOC response should be about 30% less than the actual propane concentration, and the CH_4 response should be equal to the earlier zero response. Record the stable responses on Tables 5 and 13. (If the analyzer contains an NMOC subtraction board, record the stable NMOC responses and disregard the TOC response.)

17. Determine the TOC channel's response (or the NMOC channel's response if the analyzer has the NMOC subtraction board) to two or more additional concentrations of the propane standard spaced approximately equally over the analyzer range. Record the stable responses (from the recording device) on Table 5. Using a calculator, perform a least squares linear regression of the channel's response (to propane and zero standards) and the corresponding propane calibration concentrations. The calibration concentrations should be in units of ppmC and entered into the calculator as the independent variable X and the channel's response should in units of the recording device and entered as the dependent variable Y. A correlation coefficient (r) of 0.9996 or better verifies that the response is linear. (If the response is not linear, plot the data and determine if an error has been made in data entry or in determination of calibration concentration.) Obtain the slope and intercept of the regression and record the equation in the following form:

$$\text{Channel's response} = \text{Channel's slope} \times \text{Propane concentration} + \text{Channel's intercept} \quad (15)$$

where

Channel's response = Analyzer channel's reading in recording device units (see note following step 11).

Channel's slope = Regression slope in recording device units per ppmC.

Propane concentration = Calibrated propane concentration in ppmC.

Channel's intercept = Regression intercept in recording device units.

If the analyzer contains an NMOC subtraction board, enter the NMOC responses in the regression and post the NMOC channel's multipoint calibration curve equation on the analyzer's recording device and on Tables 5 and 13. If the analyzer does not contain an NMOC board, enter the TOC responses in the regression and determine the TOC calibration curve to propane. Use the slope of this curve and Equation 1 in section 3.7 to calculate NMOC responses from future TOC and CH_4 responses.

18. Record all operational parameter readings. These readings will now become the reference readings until another multipoint calibration is performed. Be certain that the station logbook, strip charts, etc., are properly annotated, dated, and initialed.

19. If level 2 zero and span checks are to be used, carry out such a check now to establish reference zero and span readings for subsequent comparison. (See section 2.0.9.1.3 of reference 10 for definitions and additional information in level 1 and 2 zero and span checks.)

6.6.2 Level 1 Zero and Span Check

The following level 1 zero/span procedure (2-point calibration) is similar to a multipoint calibration except that only the zero air standard and one upscale standard are used. These responses are needed to calculate the new calibration curves, which should be used to correct subsequent monitoring data until another level 1 zero/span check or multipoint calibration is performed.

1. Follow the procedures in section 6.6.1 modified as follows.

   (a) Record responses on Tables 6 and 13.

   (b) After step 6, determine the zero drift in the CH_4 and TOC channels (Equation 4, section 3.8). If drift exceeds about $\pm$ 3%, determine that the CH_4 and TOC channel's electronics have not drifted (see the instruction manual) and evaluate the zero air system for possible contamination.

   If the analyzer contains an NMOC subtraction board, determine the zero drift in the NMOC channel after step 6. If drift exceeds +3%, perform step 7 and make adjustments. If drift is less than $\pm$3%, skip step 7.

   (c) After step 10, determine the span drift in the CH_4 and TOC channels (section 3.8). If drift exceeds about $\pm$ 7%, make the adjustments in steps 11 and 12 and obtain stable responses, as in step 13.

   (d) Omit step 14, but determine the slope and intercept of the CH_4 and TOC channel's level 1 calibration curve.

   Post the level 1 calibration curve on Tables 6 and 13 and on the analyzer's recording device.

   (e) After step 16, determine the TOC channel's response to propane and calculate the new TOC slope to propane. If the analyzer contains an NMOC board, determine the NMOC response to propane and determine the level 1 calibration curve.

6.7 TROUBLESHOOTING

The manufacturer's instruction manual covers this subject under the same heading. Additional comments follow.

6.7.1 Preliminary Investigations

Operational problems such as slow response to standards, inability to balance channels' responses, long stabilization periods, frequent flame-outs, or low sensitivity indicate the potential need for in-depth troubleshooting. Prior to undertaking in-depth troubleshooting procedures, a preliminary investigation is recommended to rule out variations in operational parameters.

1. Check that all pressure gauges on the analyzer are set to the specifications stated on the Manufacturer's Final Data Sheet (or to the specifications stated in section 6.5.1.6 if a manufacturer's data sheet is not available). If the analyzer has been operating properly for several months, ensure that pressure gauges are set to the readings recorded during the most recent multipoint calibration when analyzer operation was satisfactory.

2. Inspect the hydrogen source and hydrogen filters (located outside of the analyzer) for proper operation.

3. Inspect the sample filter and replace if dirty. Replace the sample line leading to the analyzer if particulate buildup is noticeable.

4. Run a chromatogram. If the chromatogram has changed since the last multipoint calibration, measure all flow rates in the analyzer and adjust to the proper specifications. Significant changes in flow may indicate a leak (slider valves may need replacement every 6 months) or an obstruction. Follow guidelines in the instruction manual.

5. If flow rates are within specifications, the gate timing may need adjustment (see section 6.5.4).

6. If columns are found to be deactivated, as indicated by the loss of separation, replace them with new columns rather than trying to reactivate the used ones.

SECTION 7

COMMENTS ON THE BYRON 233 THC/CH_4/CO ANALYZER

The Byron model 233 analyzer was not evaluated in the 1979 NMOC analyzer study (9); thus, augmented procedures to supplement the analyzer's instruction manual are not reported here. Conversations with the manufacturer have produced comments on general guidance which are reported here in lieu of augmented procedures. (NOTE: The Byron model 404 was evaluated in the 1979 study.)

7.1 PRINCIPLE OF OPERATION

The analyzer was designed to fulfill the requirements of the Federal Reference Method for determination of hydrocarbons corrected for methane (Appendix E, Part 50, Title 40 of the Code of Federal Regulations). A brief summary of the Byron 233 operation follows.

A measured amount of sample is injected directly into the FID to measure TOC concentration. Following the TOC measurement, a second, separate sample is injected into a stripper column to separate CH_4, CO, and CO_2 from the heavy organics. A second column then separates CH_4 from CO and CO_2 prior to injection into the flame ionization detector where the CH_4 concentration is measured. The CH_4 concentration can then be externally subtracted from the TOC concentration to obtain a measure of the NMOC concentration.

7.2 GENERAL COMMENTS

1. Support air supplied to the analyzer is used as carrier air, FID burner air, and valve actuation. This air must not contain more than 0.1 ppmC TOC or more than 0.1 ppm CO + CO_2.

2. The hydrogen supply must be ultra-high purity or better (contains no more than 0.1 ppmC TOC).

3. The hydrogen flow system can be leak-checked as follows.

   (a) Remove the hydrogen restrictor from the methanizer and cap the tubing.

   (b) Increase the analyzer's hydrogen regulator to the maximum position.

(c) Supply hydrogen to the analyzer's H_2 inlet at 30 psi. Shut off the hydrogen supply.

(d) Any decay in the analyzer's hydrogen pressure gauge reading in 30 minutes indicates a leak.

(e) The leak must be located and repaired.

4. Prior to ignition of the hydrogen flame, increase the hydrogen pressure about 5 to 10 psig higher than recommended for normal operation. After the burner has been lighted for at least 10 minutes, reduce hydrogen pressure to specifications.

5. Whenever the support air is changed, check the span response.

6. Moisture will deactivate the molecular sieve column. The column should be reactivated every 6 months.

SECTION 8

GENERAL COMMENT ON THE MELOY HC 500-2C FID HYDROCARBON ANALYZER

The Meloy HC 500-2C was included in the 1979 hydrocarbon analyzer evaluation (9). After the study was completed, the manufacturer indicated the analyzer's detector would be redesigned. This major change in the analyzer reduces the usefulness of augmented procedures for operating the original analyzer; therefore, no procedures are reported here.

The manufacturer has been requested to supply information on the modified analyzer; however, the information was not available in time to be included in this TAD. Users of this analyzer should consult the manufacturer for recommendations.

SECTION 9

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